DIRECT COAL LIQUEFACTION UNDER AMBIENT CONDITIONS

FINAL REPORT FOR ENERGY, MINES AND RESOURCES CANADA

BY

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SUMMARY

The novel technology of liquid clathrate solvent extraction has been successfully applied to both Western and Eastern Canadian bituminous coals of medium rank.

In experiments at 70°C and one atmosphere, the yield of liquid product (pyridine soluble) for Devco, a (marine) Cape Breton coal, was 32 ± 2 per cent, and for an A bituminous Cretaceous coal (Fording Mines, British Columbia) 22 ± 2 per cent. The principal clathrate system used was based on the tetrapropylammonium triethylaluminum iodide salt system. Parameters of extraction time, efficiency of solvent stripping (by batch, sequential and continuous methods), and of coal quality were varied.

Importantly, the pyridine soxhlet solubility of the same two coals was 8.9 and 9.5 per cent respectively.

A non-destructive reasonably reproducible workup procedure demonstrates that the bulk of the extracted material falls into the asphaltene (pyridine soluble) class with lesser amounts of chloroform and toluene soluble material consistent with a physical extraction process. In agreement, highly polar low rank sub-bituminous coals give very low net extraction yields in the absence of upgrading, though (long term) persistence of the clathrate phase in the presence of these coals is observed.

Exploratory initial experiments on homogeneous upgrading in the presence of one atmosphere of hydrogen and selected organometallic complexes show positive indications in yield and aliphatic/aromatic ratio.

In projection, techniques have been established for the spectroscopic and analytical exploration of both coal structure, and enhancement of *in situ* upgrading, as proposed for Phase II of the study. Promising indications of autocatalytic activity of the Devco coal, and even higher yields (*ca.* 50%) employing sequential clathrate extraction are among the results in this Phase I report to be pursued in subsequent work.

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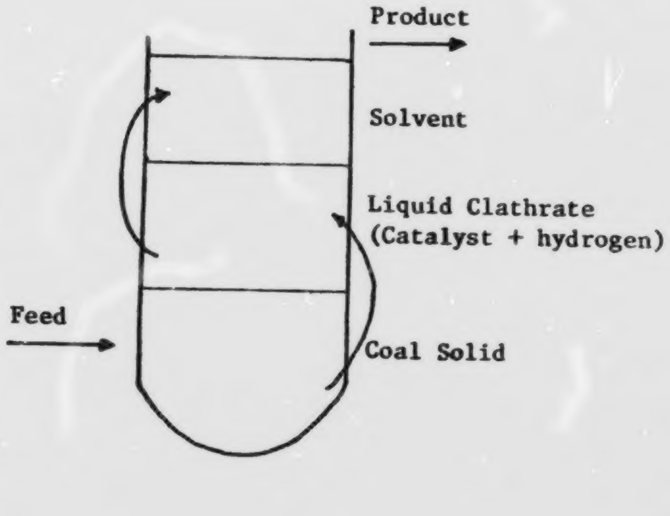
1. INTRODUCTION

1. THE CLATHRATE CONCEPT

The basic premise for exploring novel technologies for coal conversion lies in the growing concensus that adverse thermodynamic (energetic) and technological considerations are present in high temperature coal hydroliquefaction, extraction and gasification processes.

Consequently, in the proposal for this contract, it was argued that a combination of the enhanced dissolving power of aromatic solvent-salt phases, known as liquid clathrates, could be used to achieve mobilization of the coal solid at lower temperatures. Moreover, since such phases can co-exist with a solvent phase, it is possible to strip product from the clathrate phase with a collector solvent and to incorporate an upgrading catalyst into the working phase. A brief introduction to liquid clathrate behaviour is provided in Appendix I.1.1.

Conceptually, the approach is illustrated by the diagram below:



The clathrate-solvent systems were discovered by Professor J. L. Atwood, University of Alabama. Continuing mutual research collaboration between the Victoria group, and the University of Alabama has allowed his results to be used on a confidential basis in the work described in this report. Employing a series of Eastern marine coals, he has communicated that a forty per cent net transfer to the liquid phases (clathrate and stripping solvent) has been achieved by combined dissolution and *in situ* upgrading.

2. BACKGROUND

Current crude oil and natural gas costs have adversely affected the research and devlopment thrust on syn fuel technology in the short term, particularly in the private sector in the United States. In the medium term, utilization of coal reserves will be a significant factor in addressing two major problems facing future world development: (i) meeting energy requirements and (ii) assuring an adequate supply of feedstock to support synthetic organic industrial processes.

In terms of overall energy costs, analysis indicates that ultimate efficiency and hence comparative cost of coal-derived liquid is superior for direct or hydroliquefaction processes. However, in spite of the adverse thermodynamic factor of breaking the coal down to syn gas components, current established working technology is nearly exclusively gasification followed by Fischer-Tropsch or other catalytic reforming processes. For example, Sasol III, recently commissioned in South Africa, essentially utilizes the Lurgi gasifier technology from developments early in this century.

In coal liquefaction, numerous variations on a central theme have been developed. This central theme is the use of high temperature and pressure to mobilize the coal mass, typically 400 - 460°C, often with an overpressure of hydrogen gas or a supercritical fluid (toluene). The choice of temperature regime is not arbitrary; rather it corresponds closely to the region where the maximum fluidity (mesophase development) is observed for metallurgical coal (Marsh and Neavel, 1980). In this temperature range, the onset of extensive thermolysis of covalent bonds occurs in the organic structure of the coal, as evidenced by loss of volatile organic matter. Chemically speaking, the hydroliquefaction processes attempt to provide (i) a solvent for the fragments, (ii) repair of the free radicals formed from the broken bonds by hydrogen atom transfer from donor solvents. Hydrogenation catalysts are then employed at least in part, and occasionally exclusively, to regenerate partially reduced donor solvent. In some cases, since the catalyst is either incorporated in the reaction vessel; or is derived from the mineral matter in the coal, direct hydrogenation of the coal mass can occur.

While parameters such as solvent, temperature, catalyst, catalytic sequence and materials separation technology are varied, it could be suggested that the high temperature chemistry of processes such as SRCI and II, H-Coal, Exxon Donor Solvent and NCB (supercritical extraction) have much more in common than their engineering differences might suggest. Technical difficulties have plagued these processes, particularly high temperature/pressure handling problems, and at this date, in view of escalating costs, few are being actively pursued.

It is in this latter context that novel technology adopting entirely new chemical and physical approaches to coal conversion becomes appropriate. Our contention in undertaking ambient liquefaction with *in situ* upgrading using the clathrate approach is that the project represents one realization of such appropriate chemistry that will constitute the key to economic coal liquefaction in the future.

3. RATIONALE

Turning now to examination of the advantages of coal dissolution at low temperature and pressure, two distinct areas can be identified:

A. TECHNICAL ADVANTAGES

(i) Reduced energy consumption in heating and pressurization,

(ii) Reduced capital cost of process equipment,

(iii) Reduced corrosion and materials handling problems,

(iv) Advantage of a continuous extraction process for a "skimming option",

(v) Upgrading prior to extensive thermolysis of coal structures.

General application of the liquid clathrate/catalysis concept is the other major technical attraction: (a) "Locking-in" the hydrogenation process in the clathrate phase gives an immobile low-loss homogeneous catalysis that occurs after dissolution. High temperature coal liquid, biomass distillate, bitumen (syncrude) or heavy oil could be introduced into the clathrate in a two phase liquid-liquid reactor system. (b) Materials separation problems are critical to the success of other coal conversion processes of specific interest in Canada, for example the co-processing of bitumen and low rank coal (Kelly, 1981 and Moschopedis *et al*, 1980). Potentially, treating the crude product with a clathrate/collector solvent system could achieve de-ashing under relatively mild conditions.

B. COAL STRUCTURE

From a more strategic view point, design of appropriate conversion technologies requires as much detailed knowledge of coal structure as can be obtained, particularly the location and reactivity of bridging or linking groups, *i.e.* ether, ester and substituted methylene units. In the last decade, analytical methodology, particularly NMR, GC, LC, GPC and various MS techniques, has reached the stage where such investigations are feasible. A major drawback has been sufficient non-destructive dissolution of the coal mass to permit structural elucidation. Direct solvent extraction provides a limited percentage of the organic material albeit with interesting results. For example, chloroform-methanol extracts, containing 3, 4 and 5 ring polycyclic aromatic compounds have been used to trace the diogenic pathways of triterpenoids in Australian brown coal (Chaffe and Johns, 1983).

The extensive dissolution achieved by the clathrate technique potentially provides a route to more representative samples that will provide information on the structure and properties (molecular weight, solubility, functional groups) of larger organic sub-units.

In this context it is important to distinguish low temperature physical dissolution from both (1) controlled high temperature pyrolysis in either donor solvents such as tetralin or in inactive solvents, *e.g.* pyrene (Derbyshire and Whitehurst, 1981) and (2) chemically-mediated dissolution. Examples of the latter technique include both base and acid-catalysed processes. The most common base-catalysed process, often termed reductive alkylation utilizes alkalai metals (Hardy and Stark, 1982) often with an aromatic carrier. Acid catalysis has employed both protic depolymerization, *e.g.* sulphuric acid and phenol (Darlage and Bailey, 1976) and Lewis acids such as zinc chloride (Salim and Bell, 1982).

Such procedures yield valuable information on coal structure once the chemical or thermal pathway to the isolated fragment has been deduced. The value of the clathrate isolation of substructures is to provide complementary and unifying information that will contribute to the interpretation of data already in hand from these other studies.

4. THE PROGRAMME OF WORK

In the proposal for S.S.C. Z5ST-23440-2-9100, the following general objectives were advanced, consistent with the foregoing BACKGROUND and RATIONALE and relating specifically to a three-year programme:

Objectives

- To investigate the dissolution of coal solid at room temperature and pressure in a novel solvent system designated "liquid clathrate".
- To investigate the efficiency of stripping coal liquid from the "liquid clathrate" phase with solvent.

- To determine the efficiency of the process for high and medium volatile bituminous and for sub-bituminous Western Canadian coals.
- To evaluate clathrating media that incorporate hydrogenation catalysts for *in situ* upgrading in the coal liquefaction process.
- To apply clathrated catalysts to upgrading of heavy liquid fuels of diverse type.
- To determine the physical and chemical properties of hydrocarbon product from the above multi-phase processes.

In the light of these objectives, the following tasks were advanced for the first two phases:

Summary of Tasks

Phase I:

1. Section and characterization of B.C. coal samples.
2. Direct liquefaction in established clathrate/solvent systems.
3. Clathrate and solvent recovery.
4. Overall yields in the collector (solvent) and clathrate phases.
5. Elemental analysis and solvent partition (oil/asphaltene) of coal liquid product.
6. Molecular weight distribution (GPC and vapour phase osmometry).
7. Assessment of new (stable) clathrate salt combinations.
8. Comparison with Alberta and standard (Eastern) coals.

Phase II:

9. Clathrate phase-upgrading. Homogeneous catalysis.
10. Analysis of upgraded liquid, GPC, HPLC and GC/MS (solvent phase). Distillation ranges.

11. Synthesis of ionic clathrate-compatible transition metal complexes.
12. The application of clathrate catalyst working phases to heavy oil/coal liquid/bitumen upgrading.

5. STRUCTURE OF THE REPORT

Examination of the objectives of the initial phase indicates several basic areas of activity. These have dictated the organization of the Results section of the Report as follows:

Section II.1. COAL/CLATHRATE DISSOLUTION

The primary objective was the confirmation and demonstration of the physical phenomenon of clathrate dissolution as it applied to Western Canadian coals. Implicit in the tasks related to this objective was the development of a non-destructive workup procedure that would allow both the characterization and consistent (gravimetric) estimation of the yields of dissolved material.

Section II.2. COAL SURVEY

Several of the tasks related to both the geology (marine Eastern versus non-marine Western) and the rank (British Columbia samples) of the coals that were tested. Both of these parameters have been addressed and are reported in this section.

Section II.3. CHARACTERIZATION OF COAL LIQUIDS

Assessment of the derived material began with general properties (molecular weight, analyses, and solubility) and was extended to discrete spectroscopic and chromatographic information on the organic chracteristics as the project developed.

Section II.4. CATALYTIC HYDROGENATION ('UPGRADING')

As the contract proceeded, an increased emphasis on clathrate design specifically in relation to catalytic hydrogenation was indicated. Initial results on these tasks are reported in this section.

II. RESULTS AND DISCUSSION

1. COAL/CLATHRATE DISSOLUTION

A. INTRODUCTION

Phase I of the project was undertaken to investigate the novel solvating effect of the clathrate medium on bituminous coals and to establish an effective methodology for product distribution analysis. The initial stages required the establishment of techniques for the synthesis of the clathrates (Appendix II.1.1), procedures for the treatment of the coal with the clathrate (Appendix II.1.4) and procedures for the extraction and evaluation of the yield of soluble material (Appendix II.1.2). The establishment of these techniques permitted the investigation of factors affecting the process.

The overall effectiveness of the dissolution process was monitored by the yield (*i.e.* weight) of soluble material derived from the coal on treatment with the clathrate. Further evaluation of the soluble material is underway and planned as a significant emphasis of Phase II, but preliminary data are presented in the following sections. In order to compare the effects of various parameters a measure of the reliability of the yield data was established by determination of the reproducibility of the results. Investigations of different coals and clathrates were undertaken and results presented below. Investigation of operating parameters which could affect the dissolution was also commenced. Three types of extraction procedures were established, *i.e.* sequential, batch and continuous. In the sequential procedure (Appendix II.1.3) after a specified time a portion of the toluene layer was removed and replaced by fresh toluene. This procedure was used to investigate the effect of prolonged exposure to the clathrate with extraction into replenished toluene. In the batch procedure (Appendix II.1.4) after a specified time the extraction was stopped by quenching the clathrate. In this way the effect of time on a fixed system was evaluated. In the continuous procedure (Appendix II.1.5) the material extracted into the toluene layer was continuously removed so that the clathrate was always in contact with fresh toluene. A list of the trials conducted, subsequent to the establishment of satisfactory evaluation procedures, is given in Appendix II.1.6 (Table 1a).

The batch procedure was found to be effective for the extraction process and reasonably reproducible (see Section II.1.B.a.ii). This procedure was used to examine the effect of variation in the volume of clathrate (Section II.1.B.c.xii), the nature of the clathrate (Section II.1.B.ii), the type of coal (Section II.1.B.c.v). Similarly the batch procedure was used to examine the effects of various catalytic upgrading schemes as discussed in Section II.4.

B. RESULTS AND DISCUSSION

a) Reproducibility and Replication

i) Determination of Yield/Mass Balance

The yield of soluble material was determined as was the weight of coal-derived material which could be dissolved after treatment of the coal with the clathrate. This was determined by removal of the solvent after the dissolution process.

After treatment of the coal with the clathrate system three layers were formed, *i.e.* toluene, clathrate and residue. The procedures initially chosen for the extraction of soluble material from these phases are described in Appendix II.1.2.b. However these procedures were unsatisfactory as the total weights determined after dissolution and solvent removal, when combined with the weight of coal residue, far exceeded the original weight of the coal sample (10 g of coal yielded 15 - 20 g of solubles and residue). Clearly excessive contamination from decomposition of the clathrate, by alumina and alkyl ammonium salts, contributed to these weights.

A more satisfactory procedure was developed and is described in detail in Appendix II.1.2.a. This procedure yielded better overall mass balances (10 g of coal yielding 10 - 13 g of soluble and residue material) than with the initial procedure. This procedure gave rise to five soluble fractions, *i.e.* toluene solubles, chloroform solubles from the clathrate and the residue and pyridine solubles from the clathrate and the residue.* The determination of the yield of soluble material requires that contamination of each of the residues after solvent removal be reduced to a minimum. Solvent removal is described in Appendix II.1.7. Complete removal of toluene and chloroform was accomplished by standard techniques. The bulk of the pyridine was removed by similar methods and these samples exhaustively dried on a vacuum line (Appendix II.1.7). However this treatment failed to remove all traces of pyridine, as indicated by NMR, and work is still in progress in this area (Appendix II.1.9). Contamination of the samples with small amounts of pyridine preclude the determination of aromatic/aliphatic proton ratios and result in uncertainties in the overall yield data (although the level of contamination is small). The NMR of the soluble materials do not contain resonances characteristic of the alkyl ammonium salts and thus are free from such contamination. Similarly determination of the % ash (see Appendix II.1.14) in the soluble fractions do not indicate significant contamination by non-organic materials. In Table 1.1 per cent ash data are given for various samples derived from Fording K-seam experiments. These data are typical and more extensive data are given in Appendix II.1.b, Table 2. The per cent ash in the fractions which, after treatment with the clathrate, are soluble (used in yield calculations) are small (1 - 1.5%). However the per cent ash in the residues (insolubles) are relatively large and variable.

---

*In the tables, solubles derived from the coal residues are designated B and solubles derived from the clathrate designated C. In most instances weights of both pyridine soluble fractions are combined.

Table 1.1. % Ash analyses for Fording K-seam.

Treatment	% Ash[a]	Range[b]
Untreated	3.46	3.35- 3.56
Pyridine solubles, B fraction	1.27	---
Pyridine solubles, C fraction	1.36	---
Pyridine insolubles, B fraction	6.72	3.40-11.12
Pyridine insolubles, C fraction	6.79	4.04-11.17
Pyridine solubles, soxhlet extraction	0.00	---

---

[a] average value where appropriate

[b] only where more than one sample determined

Overall mass balance data for representative samples are presented in Table 1.2. More complete data are given in Appendix II.1.6.

Table 1.2. Representative mass balance data (weights in grams).

Expt. #	Coal	Conditions	Wt. of Coal	Wt. of Solubles	Wt. of Insolubles	Total Wt. Recovered
10-7	Devco	20 hr, 70°	10.00 g	3.262	8.126	11.388
2-34	K-seam	20 hr, 70°	10.00 g	2.328	10.873	13.201
2-40	K-seam	4 hr, 70°	10.00 g	1.147	9.410	10.557
11-10-3	Devco	18 hr, soxhlet	10.00 g	0.887	9.805	10.692

The overall mass balance data are affected by contamination of the coal residue. Entrapment of pyridine or clathrate decomposition products into the residue are likely sources of contamination. Such contamination may result from incorporation of clathrate and/or pyridine into the residue. Entrainment of pyridine has been observed previously (Larsen *et al*, 1984) and has also been observed in direct extraction of the coal with pyridine in this project. Per cent ash data (large ash values indicate entrapment of clathrate decomposition products into the residue) are presented in Table 1.1. These data are variable and, together with the reported entrainment of pyridine in the coal, are sufficient to explain the variability in the mass balance data indicated in Table 1.2. Samples of the residues from several coals have been subjected to petrographic and microscopic analysis at the University of Regina as discussed in Section II.2.B.

ii) Replicate Trials

The sequential extraction trials were carried out over extended time periods and replicate studies were not attempted. However, as discussed in Section II.1.B.b (following), all trials showed the same trends with respect to the toluene soluble material.

Replicate trials were conducted by the batch procedure. Table 1.3 presents data for five replicate trials conducted on the K-seam coal. The overall standard deviation reported for the total yield of soluble material is somewhat better than that for each of the component solutions. The majority of these replicate trials were conducted soon after the adoption of the procedure described in Appendix II.1.2a and further replicate trials will be conducted in the next phase of the project.

Table 1.3. Replicate trials on K-seam coal; 20 hour extraction with 100 ml clathrate (weights in grams).

Expt. #	Wt. of Tol. Solubles	Wt. of $CHCl_3$ Solubles		Wt. of Pyr. Solubles†	Total Wt. of Solubles
		B*	C*		
2-21-1	0.128	0.069	0.130	2.057	2.384
2-21-2	0.098	0.046	0.123	2.132	2.399
2-21-3	0.131	0.048	0.106	1.685	1.970
2-21-4	0.186	0.038	0.146	1.816	2.186
2-34	0.089	0.031	0.089	2.171	2.380
Mean	0.126	0.046	0.119	1.972	2.264
Standard Dev.	0.038	0.014	0.022	0.212	0.186

---

*B refers to extraction of the coal residue.
C refers to extraction of the clathrate.

†Weights of pyridine solubles derived from the coal residue (B fraction) and the liquid clathrate are reported as combined weights.

b) Sequential Extractions

In the early stages of the project a series of trials were conducted, over extended time periods, in which half the toluene layer (50 ml) was drawn off and replaced by fresh toluene at specific time intervals. Details of the procedure are given in Appendix II.1.3.

i) Time Variation of Toluene Solubles

The effect of prolonged exposure of the coal to clathrate was monitored through the amount of material which dissolved in the toluene layer. The results of several trials are presented graphically in Appendix II.1.8.a. All trials conducted with coals which gave toluene soluble material (Hat Creek and Forestburg gave very little material) followed the same general trend. There was a fairly rapid dissolution in the early stages followed by a much slower dissolution which continued for many days.

Proton NMR was used to monitor the aromatic/aliphatic proton ratio of the toluene soluble material. These data, Appendix II.1.8.b, showed a steady increase in the aromatic protons (relative to aliphatic) in the initial stages of the dissolution followed by a general decrease in the ratio for material extracted later.

ii) Variation with Coal

Trials were conducted with K-seam, Merritt, Hat Creek, Forestburg and Telkwa coals using the sequential procedure. Results of representative trials for each coal are given in Table 1.4.

Table 1.4. Sequential extractions on various coals (10 g).

Coal	Time[a]	Toluene Solubles (g)	Pyridine Solubles (g)
Hat Creek	Several days	0[b]	0[b]
Forestburg	Several days	0[b]	0[b]
Telkwa	5 days	0.287	0.394
Merritt	7 days	0.343	0.393
K-seam	6 days	0.772	1.470

---

[a] At time of termination of extraction less than 0.02 g of material (toluene solubles) was being extracted per day.

[b] The toluene and clathrate layers were not coloured by these coals.

The variation of yields with the coal is quite dramatic. The variation is discussed in Section II.2.C.b. Comparing the data in Table 1.4 with those in Table 1.9 (soxhlet extraction) it is seen that both Hat Creek and Forestburg yield low pyridine solubility values, an observation consistent with the data in Table 1.4.

c) Batch Extractions

After the early sequential trials established the general relationship between time and the extraction into the toluene layer (with periodic replacement of toluene), it was decided to continue further experiments on a batch basis, since many more data could be acquired in this way. The procedure used for the batch extractions is described in Appendix II.1.4, standard extractions used 10g of dried coal, 100 ml of clathrate and 100 ml of toluene.

i) Variation with Time

Trials were conducted using either a 4 hour or 20 hour extraction procedure. Representative data for K-seam and Devco coals are given in Table 1.5.

Table 1.5. Comparison of 4 hour and 20 hour batch extractions.

Coal	Time (hr)	Toluene Solubles (g)	$CHCl_3$ Solubles: Coal Extract.	$CHCl_3$ Solubles: Clathrate Extract.	Pyridine Solubles	Total Solubles
K-seam	4	.015	.008	.035	1.089	1.149
K-seam	20	.089	.031	.089	2.171	2.380
Devco	4	.048	.023	.077	1.629	1.777
Devco	20	.120	.027	.149	2.966	3.262

The data are consistent with the general trends established in the sequential extraction trials, with each fraction showing a significant increase in solubles with longer exposure to the clathrate. It should also be noted that comparison with the data for the sequential trials (Appendix II.1.8.a) indicate that replacement of the toluene appears to enhance the amount of toluene soluble material derived in a given time.

The standard reaction time of 20 hours was adopted for most trials. The time was chosen to provide significant dissolution and to be convenient for experimental work.

ii) Choice of Clathrate and Clathrate Stability

An extensive study concerning the effect upon coal liquid yields of varying liquid clathrate types has not been conducted. Atwood has reported using several types of clathrate in his preliminary coal extraction studies with no obvious trends occurring (Atwood, J. L., personal communication). The tetrapropylammonium iodide based liquid clathrates were chosen for the majority of the experiments in the present study for several reasons, with overall stability being the principal criterion. Eliminated from consideration were oxygen-containing liquid clathrates, which are prone to facile decomposition to oxy-aluminate species and azide-based clathrates because of the potential explosion hazard should transition metal azides inadvertently be formed. The NR_4I series of clathrates offer the advantage of high thermal stability, a direct comparison with some of Atwood's results and moderately low cost. NPr_4I was chosen since it has relatively high aromatic/anion ratio and gives simpler ^1H NMR spectra than its longer chain counterparts. Appendix II.1.10. presents ^1H NMR spectra of the $[NR_4][Al_2Et_6I]$ (R = Me, Et, Pr, Bu) series of toluene-based liquid clathrates.

Even with a liquid clathrate of high thermal stability, materials present in coal lead to some oxy-aluminate formation. The amount of decomposition is low, but is sufficient to affect yield of solubles, since these species may enter the toluene phase (see Appendix II.1.2.a for method of treating toluene phase). Through using the toluene-d_8 based liquid clathrate, ^1H NMR spectra of the clathrate decomposition product have been obtained (details of preparation and the spectrum are given in Appendix II.1.11). The NMR results suggest that the product is likely to be a four (Atwood and Zaworotko, 1983) or six (Atwood, Hrincir *et al*, 1983) membered ring oxy-aluminum compound of the type identified by Atwood.

The degree of clathrate decomposition (as a percentage) during coal extraction procedures will be examined in Phase II, as will the effect of certain radically different clathrates upon coal liquid yields (*e.g.* NaCl, KCl based liquid clathrates).

iii) Variation of the Amount of Clathrate

Preliminary trials were conducted by varying the volume of the tetrapropylammonium iodide based clathrate. Trials were conducted with 10 g of coal, 100 ml of toluene and varying amounts of clathrate. Data are presented in Table 1.6.

Table 1.6. Effect of variation in amount of clathrate.

			$CHCl_3$ Solubles (g)			
Coal	Vol. of Clathrate	Toluene Solubles (g)	Coal Extraction	Clathrate Extraction	Pyridine Solubles (g)	Total Solubles (g)
K-seam	50 ml	.052	.014	.107	1.512	1.685
	100 ml	.089	.031	.089	2.171	2.380
	200 ml	.065	.023	.145	2.284	2.517
Devco	50 ml	.117	.064	.093	2.154	2.364
	100 ml	.120	.027	.149	2.966	3.262
	200 ml	.068	.021	.176	2.404	2.648

These data appear to indicate that an increase from 50 ml to 100 ml of clathrate results in an increase in the overall yield. However, as the volume of toluene and the volumes in the workup procedures were not adjusted and the standard deviations for replicate trials are large (Section II.1.b.a.ii) these trials must be repeated before the results may be treated with confidence.

iv) Extraction of Coal Residue

Two trials were conducted in which the coal residue from an extraction was treated with fresh clathrate and re-extracted. Data are presented in Table 1.7

Table 1.7. Re-extraction of coal residue.

Coal	Toluene Solubles (g)	$CHCl_3$ solubles (g) Coal Extract.	$CHCl_3$ solubles (g) Clathrate Extract.	Pyridine Solubles (g)	Total Solubles (g)
K-seam					
1st extraction*	.126	.046	.119	1.972	2.264
2nd extraction	.029	.010	.037	1.703	1.772
Devco					
1st extraction*	.121	.052	.182	2.893	3.215
2nd extraction	.032	.019	.015	2.142	2.208

---

*These data are averages for several trials.

Clearly in both cases significant amounts of additional material were made soluble in the second extraction. The additional material was mostly pyridine soluble, as might have been anticipated. Further work in this area is planned as these results may indicate that improved yields of soluble material may be obtained in a system in which the coal is cycled through several extraction stages.

v) Variation with the Coal

As indicated in Section II.1.B.b extraction of Hat Creek and Forestburg coals by the sequential procedure gave insignificant dissolution in short periods (*i.e.* a few hours). Consequently work with these coals was discontinued. K-seam, Devco, Illinois #6, Quinsam and Mary Lee coals have been examined by the batch procedure. Representative data are presented in Table 1.8.

Table 1.8. Representative extractions with different coals.

Coal	Toluene Solubles (g)	$CHCl_3$ Solubles (g)		Pyridine Solubles (g)	Total Solubles (g)
		Coal Extraction	Clathrate Extraction		
K-seam	.089	.031	.089	2.171	2.380
Devco	.120	.027	.149	2.966	3.262
Illinois #6	.033	.031	.076	1.885	1.992
Quinsam	.053	.039	.052	1.030	1.174
Mary Lee (Alabama)	.083	.036	.184	2.933	3.236

Rank profiles and other parameters for each of the coals are presented in Section II.2.B. The data presented in Table 1.8 are discussed in Section II.2.C.b. Data have also been acquired on trials conducted using mixtures of Devco and K-seam coals. These data indicate that the Devco coal enhances the yield from the combined system and are discussed in Section II.4.B.d. Table 1.9 presents data for the direct dissolutions of the coals in toluene or pyridine in the absence of the clathrate (Appendix II.1.12).

Table 1.9. Soxhlet extraction of coals in 17 hours based on 10 g of coal.

Coal	Toluene Solubles (g)	Pyridine Solubles (g)
Hat Creek	.039	.286
Forestburg	.018	.349
Quinsam*	.038	.500
Telkwa	.057	.722
Devco*	.026	.887
K-seam	.085	.950
Merritt	.057	.980
Mary Lee*	.017	1.687
Illinois #6	.030	1.011

---

*20 hour soxhlet extractions

These data clearly indicate that Hat Creek and Forestburg coals are less readily extracted by pyridine than the other coals. These two coals, as noted in Section II.1.B.b, failed to colour the toluene or clathrate layer when treated by the sequential extraction procedure. The Quinsam coal also provided a relatively low yield on treatment with the clathrate (Table 1.8). There is thus a general correlation between the pyridine extraction of the coal and the yield in the clathration process. However the coals which exhibit a reasonable pyridine solubility (∿ 10%) do not give a good direct correlation with the clathrate yield.

d) Continuous Extraction

The data acquired by the sequential and batch extraction procedures indicated that the yield depended on the rate at which the solvent (toluene) was renewed. Thus a continuous extraction procedure, described in Appendix II.1.5, was devised. In this procedure the toluene layer was "continuously" replaced by toluene from which the dissolved coal derived material had been removed. A similar dependence may also exist for the clathrate phase (see Section II.1.B.c.iv) but has not been investigated.

i) Yields by Continuous Extraction

Only two trials have been conducted to date using the continuous extraction procedure. Yield data are presented in Table 1.10.

Table 1.10. Yields from continuous extraction.

Coal	Time	Toluene Solubles (g)	$CHCl_3$ Solubles (g)		Pyridine Solubles (g)	Total Solubles (g)
			Coal Extraction	Clathrate Extraction		
K-seam	20 hrs	.271	.035	.046	2.327	2.679
K-seam	4 hrs	.091	.007	.041	0.696	0.835

The data presented in Table 1.10 should be regarded as preliminary as they are the results of only one trial in each case. However, comparison of these data with the batch data for similar times (Table 1.5) clearly indicate that within the anticipated standard deviation (Section II.1.B.a.ii) the yield of toluene soluble material is increased significantly whereas the overall yield remains unchanged. These data are consistent with the trends observed for the sequential extraction trials (see Section II.1.B.6).

ii) Nature of the Toluene Soluble Material

Proton NMR spectra of the toluene soluble material are shown in Appendix II.1.13 (Figures 1, 2, 5, 6). These correspond to the material in the toluene layer in contact with the clathrate and in the toluene in the refluxing vessel for each trial. The spectra clearly indicate that the material in the refluxing vessel contains more aromatic protons than that in contact with the clathrate. Further examination of these materials is in progress. The higher aromatic content in the refluxing toluene may be the result of aromatization reactions promoted by traces of aluminum alkyls present in the reflux vessel or a partitioning of the material between the two toluene solutions. The latter may occur if the aromatic material is preferentially dissolved in the clathrate phase with only a small fraction extracted into the toluene. As the experiment continues the aromatic material would build up in the reflux vessel and fresh toluene slowly extract the material from the clathrate layer. Since this change in ratio occurs for both the 4 and 20 hour continuous extraction the effect does not appear to result from a variation in the aromatic/aliphatic ratio with the time of extraction as was reported in Section II.1.B.b.i. Further investigation of these results is in progress.

2. COAL SURVEY

A. INTRODUCTION

All coal liquefaction and solvation programmes have demonstrated that different coals can give dramatically different yields for the same reaction conditions and this system is no exception. One of the common parameters used for yield comparisons is the mean maximum reflectance ($\overline{R}_o$(max)). The mean reflectance of a coal is related to its rank as is shown in Table 2.1 (taken from Ting, 1978 and Larsen, 1981). Normally a similar relationship is found when the mean reflectance is replaced by the percentage carbon in the coal on a dry-ash-free basis. This is because both the carbon content and the $\overline{R}_o$ value increase with increasing rank. There is a range of values, however, such that two coals with the same carbon content need not have the same $\overline{R}_o$ value.

The coals of British Columbia have representatives in most of these ranks from the sub-bituminous (almost lignitic) Hat Creek coal to the anthracite found in the Klappan Deposit in the northwestern B.C. Ground Hog coal field (see Figure 2.1). Several B.C. coals have been investigated in Phase I of this programme and additional ones will be studied in Phase II. In addition to coals from B.C. several other coals have been tested. The coals selected had been the subject of several other investigations (Devco, Forestburg and Illinois #6) or had previously been investigated by the clathrate procedure in Alabama (Mary Lee coal). Another factor influencing the selection of coals was an attempt to test coals with a range of carbon content from < 50% to 90% in an attempt to investigate the extraction yield as a function of rank. Several coals have yet to be

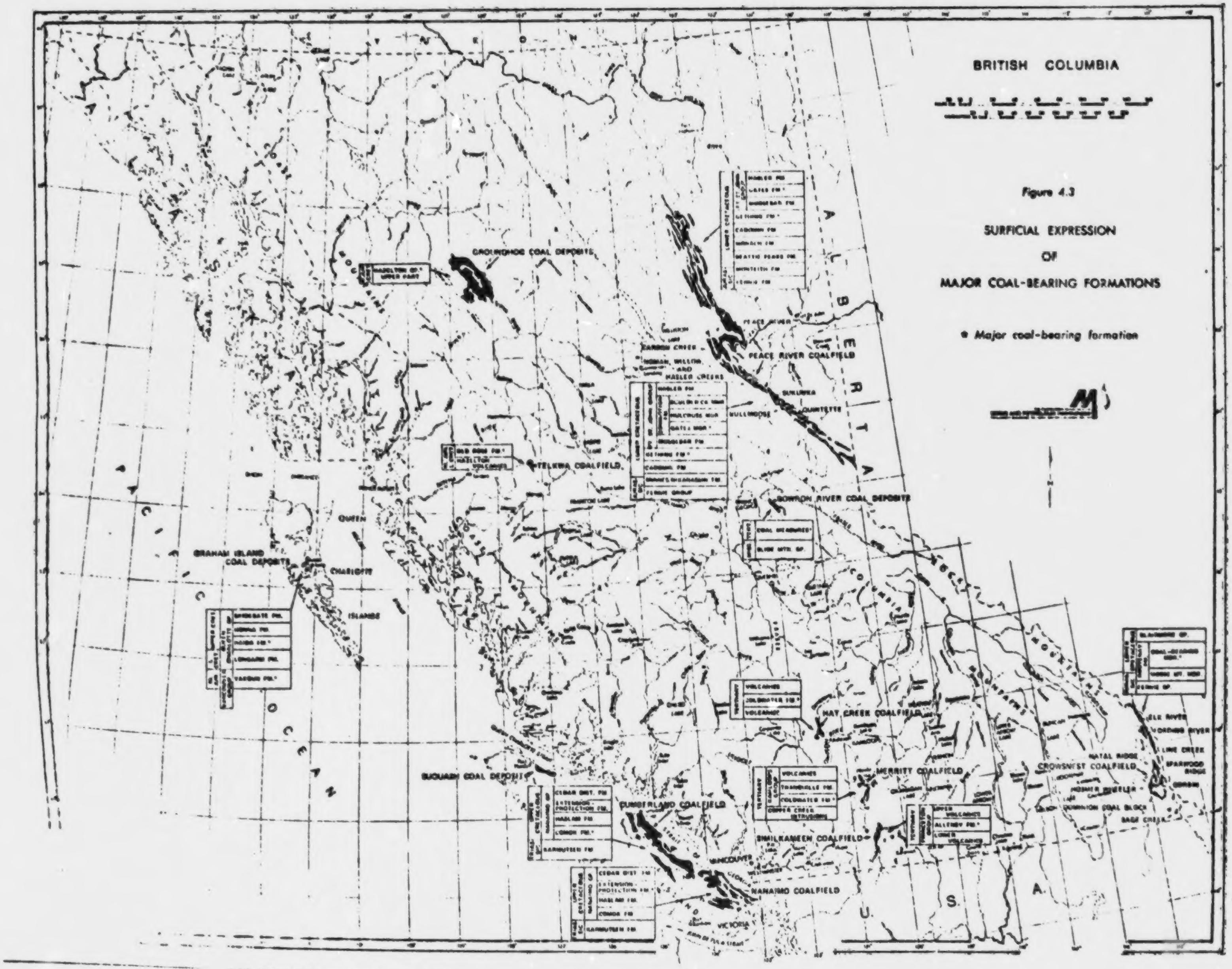

BRITISH COLUMBIA
Figure 4.3
SURFICIAL EXPRESSION
OF
MAJOR COAL-BEARING FORMATIONS
* Major coal-bearing formation
ALBERTA
U. S. A.
PACIFIC OCEAN
QUEEN CHARLOTTE ISLANDS
GROUNDHOG COAL DEPOSITS
PEACE RIVER COALFIELD
PEACE RIVER
CARBON CREEK
BULLMOOSE
QUINTETTE
TELKWA COALFIELD
BOWRON RIVER COAL DEPOSITS
GRAHAM ISLAND COAL DEPOSITS
HAT CREEK COALFIELD
MERRITT COALFIELD
SIMILKAMEEN COALFIELD
CROWSNEST COALFIELD
NATAL RIDGE
ELK RIVER
FORDING RIVER
LINE CREEK
SPARWOOD RIDGE
HOSMER WHEELER
DOMINION COAL BLOCK
SAGE CREEK
SUQUASH COAL DEPOSIT
CUMBERLAND COALFIELD
NANAIMO COALFIELD
VANCOUVER
VICTORIA
VOLCANICS
COLDWATER FM.*
TRANQUILLE FM.
COPPER CREEK INTRUSIONS
ALLENBY FM.*
CEDAR DIST. FM.
EXTENSION-PROTECTION FM.
HASLAM FM.
COMOX FM.*
NANAIMO GP.
GETHING FM.*
GATES FM.*
COAL MEASURES*
BLUE MTN. GP.
KOOTENAY
ROCKY MOUNTAINS
COAST MOUNTAINS

Figure 2.1

run to complete this survey on the basis of carbon content.

Petrographic and elemental analysis data are available for some of these coals and will be obtained for the other coals.

Table 2.1. Table showing $\overline{R}_o$(max) range and approximate carbon content of coals of different rank.

Rank (or Class)	$\overline{R}_o$(max)	%C (daf)
Wood	-	49
Peat	-	60
Lignite	0.25 - 0.4	70
Sub-bituminous	0.4 - 0.5	73
Bituminous	0.5 - 2.0	83
Anthracite	> 2.0	94

B. COMPARATIVE PETROGRAPHY OF TREATED AND UNTREATED COALS

There are several significant, if preliminary, observations resulting from the petrographic analysis of samples sent to the University of Regina. The residues from the first type of experiments did not give reliable results because of alumina contamination (Section II.1.B.a.i). The residues from samples treated by the current workup procedure (Appendix II.1.2.a) were not subject to this contamination and the information derived should assist greatly in interpretation of the data from the clathrate experiments.

Detailed information has not been received from the University of Regina but a few general observations conveyed by telephone from Dr. McDougall for inclusion in this report follow.

(a) The overall mean reflectance ($\overline{R}_o$) of the coal residue is much lower than is that of the untreated coal. This includes that of the lighter centres of the coal particles (see Table 2.2). Dr. McDougall indicated that the mean reflectance value will be only slightly different from the mean maximum reflectance of the coal.

(b) There is definite zoning evident in the individual coal residue particles. The outer rims of the particles are darker than the centres and give lower reflectance values than the centres.

(c) There is no evidence of the clathrate treatment affecting one maceral to a greater extent than another (*i.e.* the liptinite macerals are not more affected than are the inertinites).

(d) In a few instances the dark area of lower reflectance occurs in streaks across particles rather than around the rim of the particle. It is not clear if this is associated with microfractures in the coal particle or some other factor.

(e) There was a substantial rise to 20.8% vitrinite in the residue from a cold pyridine extraction of a sample of K-seam coal as compared with 13.8% vitrinite in the raw coal.

(f) A coal residue from an extraction with pyridine was clathrated (11-2-1-B) and in this case the reflectance of the centre of the particles was less than that of the rim.

Table 2.2 Mean reflectance values.

Experiment*	Coal Sample	Mean reflectance % ($\bar{R}_o$) raw coal	rim	centre	Comments
-	Merritt	0.73	-	-	Raw coal sample
-	Illinois #6	0.54	-	-	Raw coal sample
-	Devco	0.85	-	-	Raw coal sample
-	K-seam	0.72	-	-	Raw coal sample
2-22-B	K-seam	0.72	0.30	0.51	
2-23-B	K-seam	0.72	0.37	0.65	
2-26	K-seam	0.72	-	-	Cold pyridine extraction
2-28-B	K-seam	0.72	0.36	0.58	
2-29-B	K-seam	0.72			
11-2-1-B	K-seam	0.72	0.33	0.27	Note reversal of reflectance. Sample pre-extracted with pyridine.
11-2-2-B	K-seam	0.72			Light and dark streaks
9-1-B	Illinois #6	0.54			
10-4-B	Devco	0.85	0.35→0.4	0.79	Light and dark streaks
10-4-C	Devco	0.85	0.35→0.4	0.77	Light and dark streaks
10-5-B	Devco	0.85	0.42	0.75	
2-6 and 2-7	K-seam	0.68	-	-	0.45 mean R_o % of residue†

---

* Details of experiments given in Appendix II.1.6, Table 1.a.
B refers to coal residue.
C refers to residue after workup of clathrate phase.

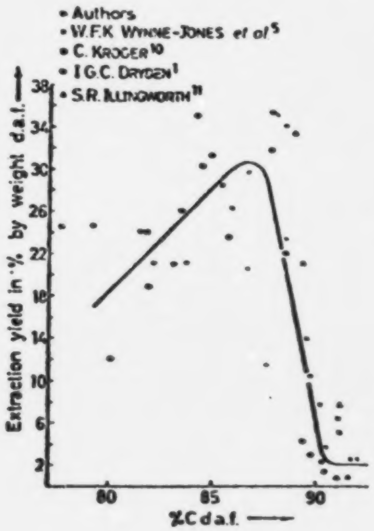
† 2-6 and 2-7 were early experiments from which the residues were contaminated with clathrate decomposition products.

C. EXPERIMENTAL RESULTS AS RELATED TO PETROGRAPHIC DATA AND COAL QUALITY

a) General

A plot of the yields from pyridine extractions of different coals as a function of carbon content (*i.e.* rank) is shown in Figure 2.2 (Larsen, 1981). The maximum at 85 – 90% carbon is also found in many other plots of coal characteristics versus carbon content (Larsen, 1981); examples are average molecular weight per cross-link, coal reactivity under "mild" conditions, coal conversion in pyrene and coal fluidity as measured by a Geisler Plastimeter.

Coals investigated in this project have covered a range of carbon content from < 50% to 87.0% (see Table 2.3). The corresponding $\overline{R}_o$ petrographic values range from < 0.45 for Hat Creek to 0.84 for Devco (Table 2.2). (Note that the Devco coal has a higher $\overline{R}_o$ value then the K-seam coal but a lower carbon content (Table 2.4).)



Extraction yield in pyridine at 115°C versus rank

Figure 2.2. Yield of pyridine extract as a function of carbon content.

Table 2.3. Analysis of coals used (in %)

Coal	C	H	N	S	Ash	Moisture
Hat Creek	45	2.8	0.7	0.39	26.6	23.5
Illinois #6	80	5.36	1.49	0.68	5.91	
Quinsam	72	4.48	0.92	0.39	11.33	4.01
Devco	73	4.65	1.57	1.69	6.83	2.86
K-seam	87	8.4	0.8	0.45	3.45	
Forestburg	59	3.71	1.26	0.50	7.48	10.0
Quinsam	60	4.75	0.88	0.38	10.15	3.66

Table 2.4. Solvent and clathrate extraction yields as a function of mean reflectance and carbon content of various coals.

Coal	$\bar{R}_o$	%C (daf)	Tol. Extr'n.	Pyr. Extr'n.	Clathrate Tol. Sol.	Clathrate Chl. Sol.	Clathrate Pyr. Sol.	Clathrate Total Sol.
Forestburg	<0.4	71	0.18%	3.50%	No significant extraction			
Hat Creek	<0.45	61	0.39	2.87	No significant extraction			
Illinois #6	0.54	80	0.30	10.1	0.33%	1.07%	18.85%	19.9%
K-seam	0.72	87	0.85	9.5	0.89	1.2	21.71	23.3
Merritt*	0.73	-	0.57	9.78	3.43	*		
Devco	0.84	81	0.26	8.87	0.98	2.18	33.02	36.2
Quinsam	-	81	0.38	4.62	0.53	0.91	10.3	11.7

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*comparable clathrate data not available.

b) Extraction Yields as a Function of $\overline{R}_o$ and %C

i) Soxhlet Extractions

Figures 2.3 and 2.4 are plots of soxhlet extraction yields as a function of $\overline{R}_o$ and of %C respectively. No trend is apparent for the toluene data. The pyridine soluble fraction increases with both $\overline{R}_o$ and %C over the range available. No data are available to indicate whether the yield decreases at high $\overline{R}_o$ or %C as would be suggested by Figure 2.2.

ii) Toluene and Chloroform Extractions after Clathration

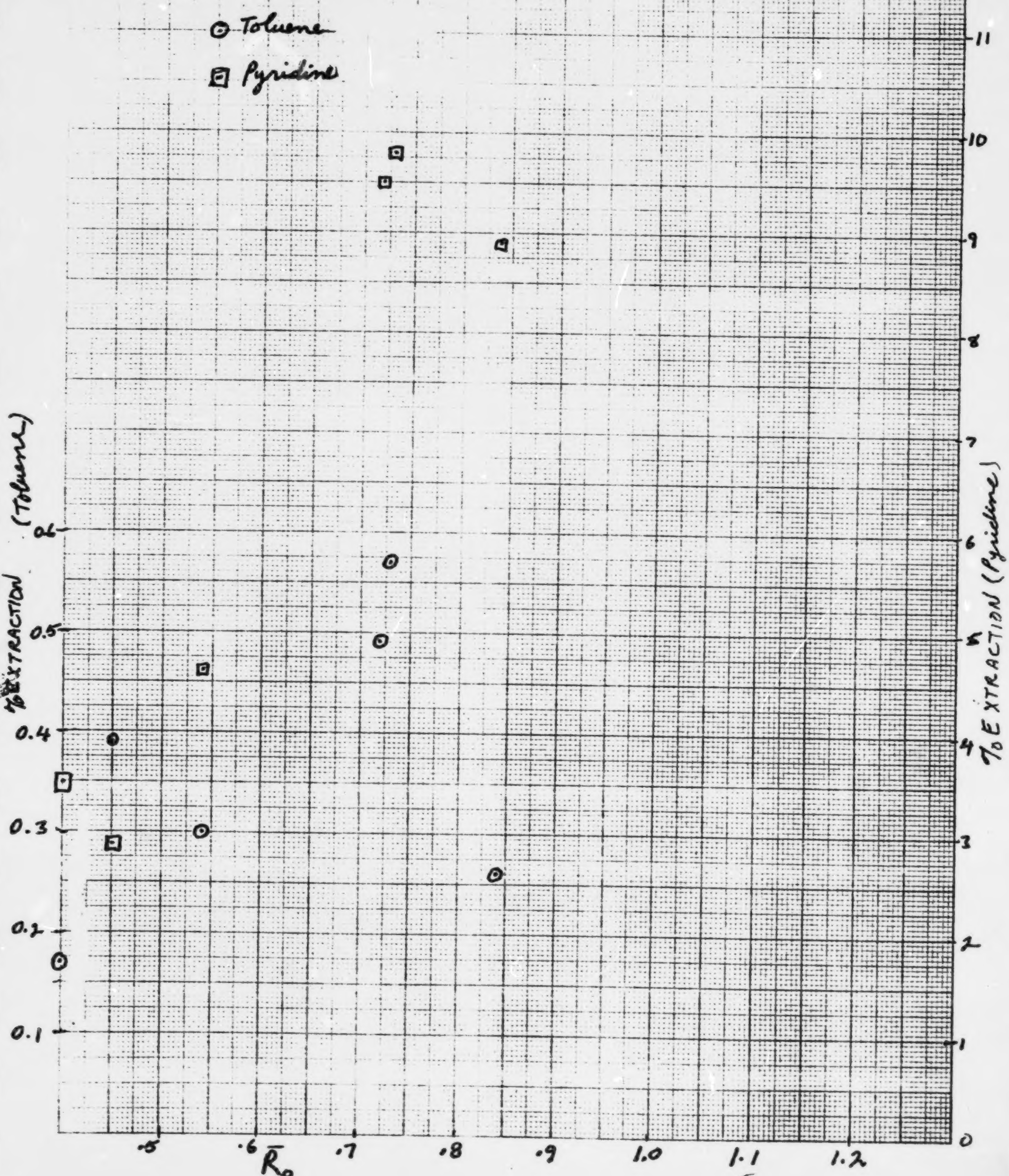
Both the toluene and chloroform soluble fractions appear to show a clear trend of increasing yields with increasing $\overline{R}_o$ (see Figure 2.5). The same data plotted as a function of %C (Figure 2.6) show considerable scatter. The yields of both these fractions are small (less than 2.2% in all cases) and more data are required before they may be treated with confidence.

iii) Pyridine and Total Extractions after Clathration

Because by far the largest fraction of material extracted from the coal is toluene and chloroform insoluble but pyridine soluble, the total extraction graph reflects the pyridine soluble trend. As with the toluene and chloroform solubles there is clearly an increase in yield with increasing $\overline{R}_o$ (Figure 2.7). Similarly the yield increases with increasing C content of the coals (Figure 2.8), although there is considerable scatter in the data. Once again insufficient data are available to indicate whether a decrease in yield is observed at very high carbon content.

FIG 2·3

Soxhlet Extractability as a Function of $\bar{R}_0$



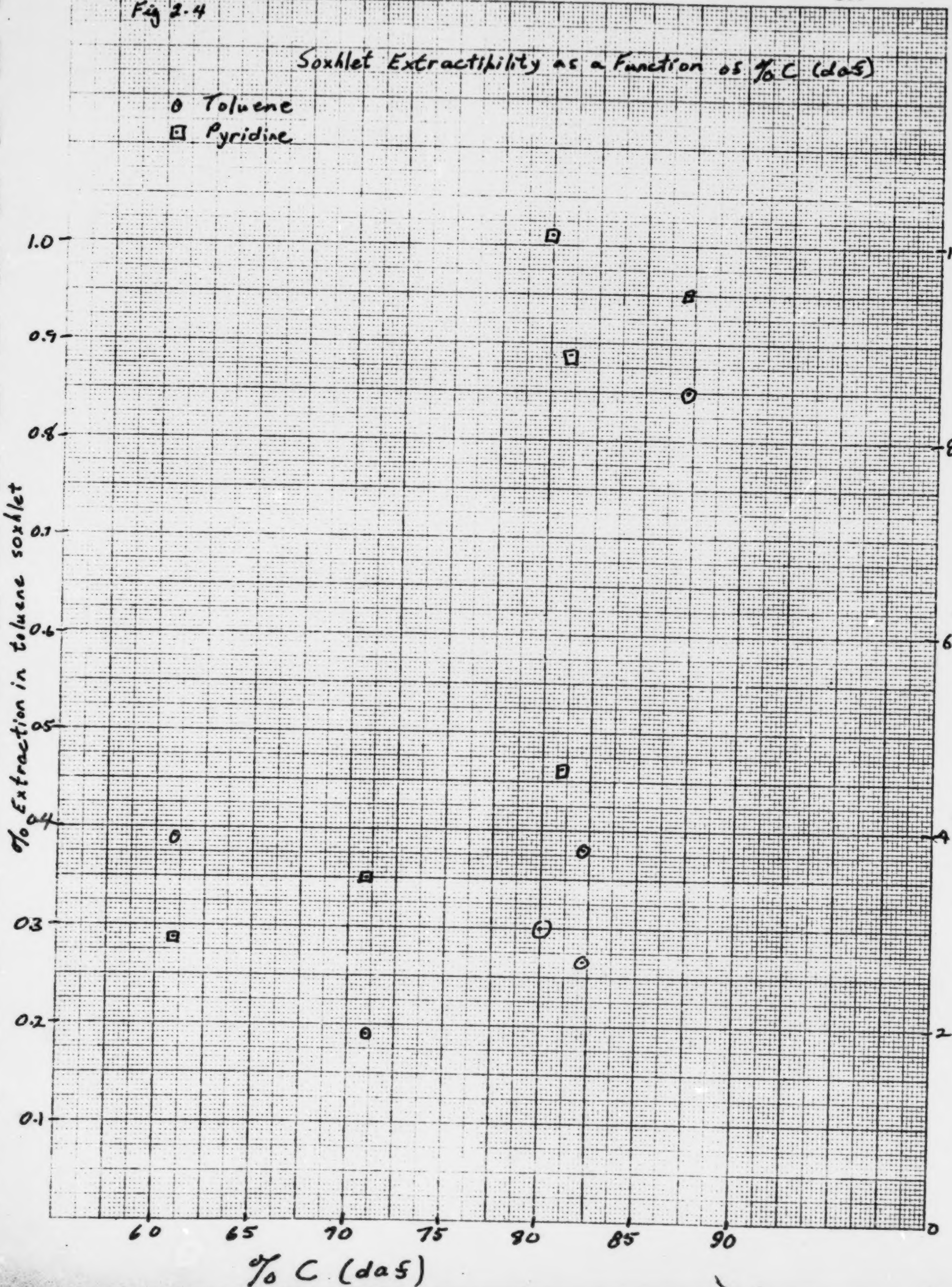
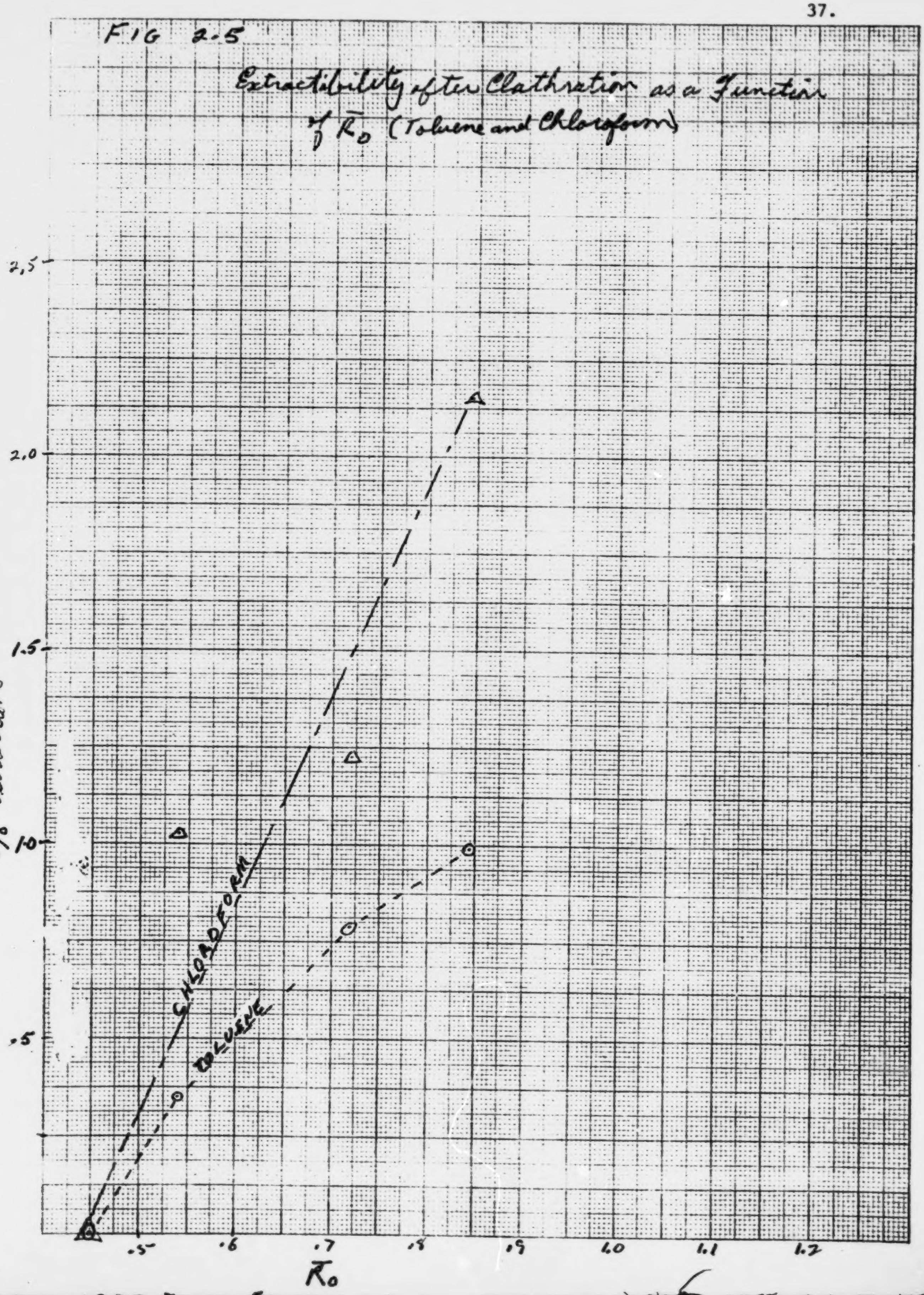


Fig 2.4

Soxhlet Extractibility as a Function of % C (daf)

FIG 2.5

Extractibility after Clathration as a Function of $\bar{R}_0$ (Toluene and Chloroform)



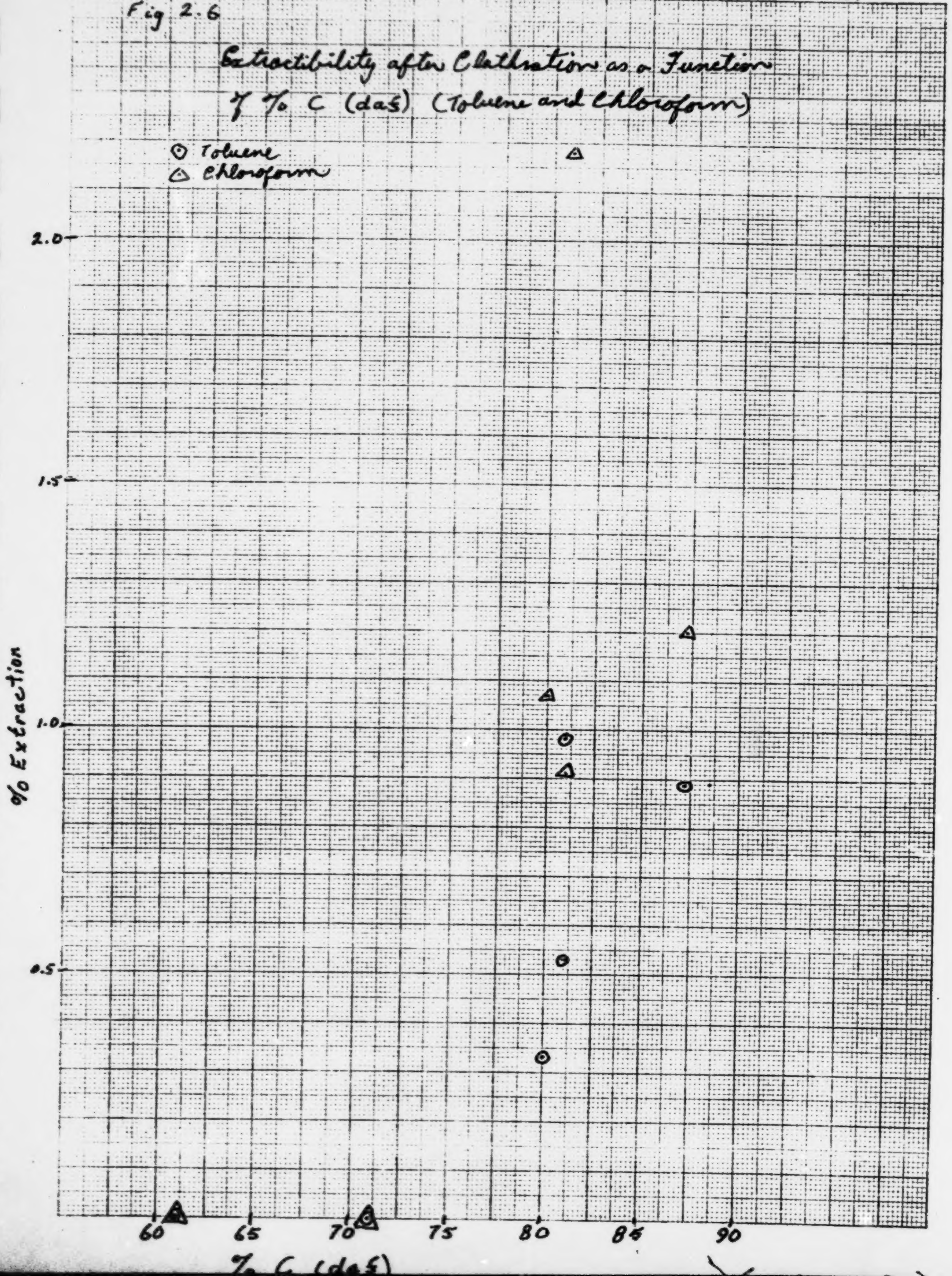


Fig 2.6

Extractibility after Clathration as a Function of % C (daf) (Toluene and Chloroform)

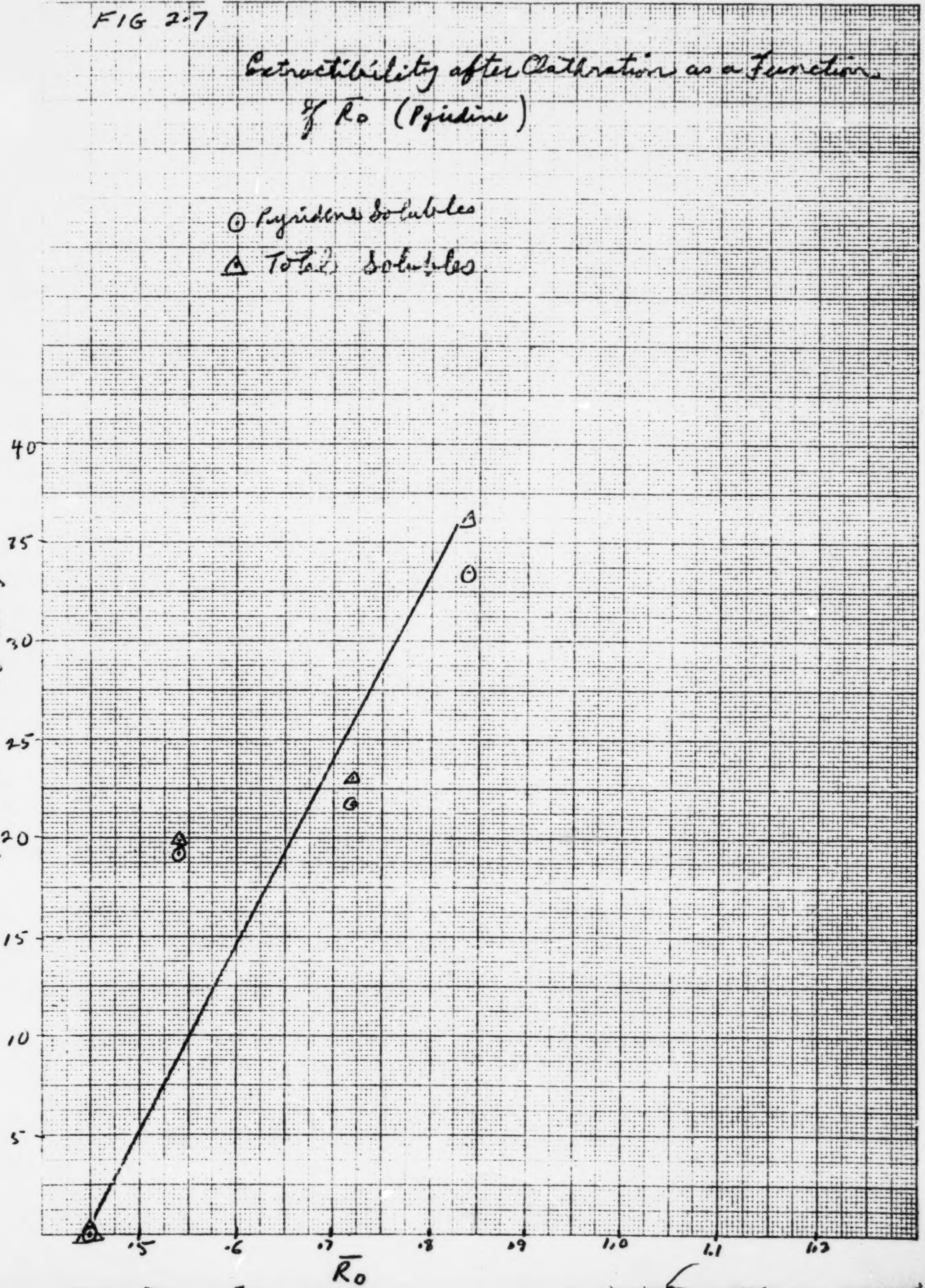


FIG 2·7

Extractibility after Clathration as a Function of Ro (Pyridine)

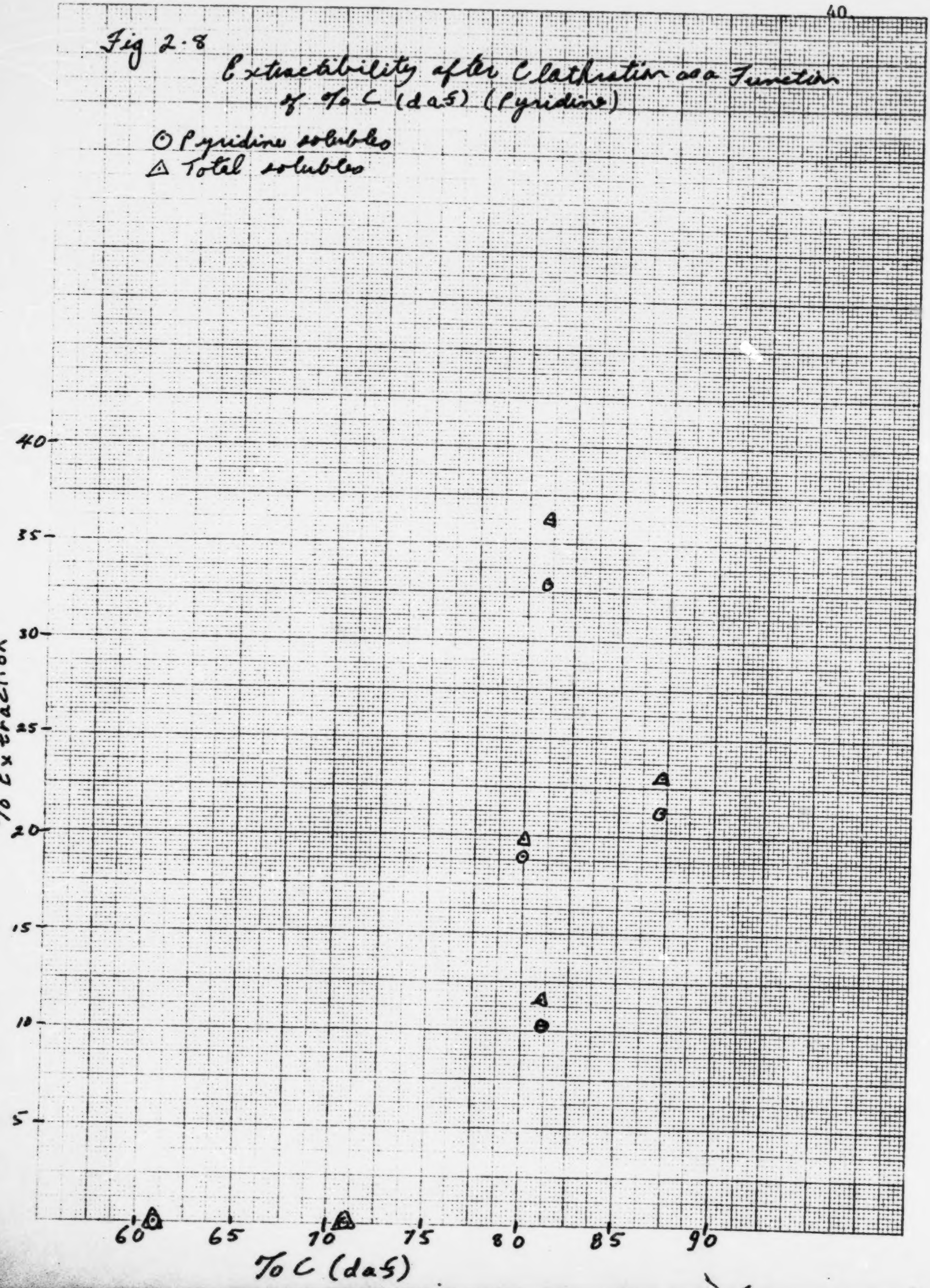


Fig 2.8

Extractibility after Clathration as a Function of %C (daf) (Pyridine)

c) Extraction Yields as a Function of Coal Quality

Experiments were run to compare oxidized and unoxidized K-seam coal. The unoxidized coal had been stored frozen under Ar for 18 months since collection and was ground under N_2 in the dry box just prior to extraction (Appendix II.2.1). Experiments 2-16 through 2-19 in Table 1b of Appendix II.1.6 give the details. The extraction yield appears to be unaffected by the degree of oxidation of the coal.

Another sample of K-seam coal was boiled in 10% HCl for 1 hr, filtered, washed several times with water and dried overnight at 80°C in the vacuum oven. This coal was then extracted with clathrate and a significant decrease in the amount of soluble material was observed although the amount of chloroform soluble material was over 8% (Experiment 2-20, Table 1b in Appendix II.1.6). The observed decrease is in contrast to the increase observed in other recent studies (Sharma and Mirza, 1983; van Bodegom, 1984) of solvent extraction. However the rank of the coals used in the present investigation is considerably higher than of the coals used by Sharma and van Bodegom. Clearly on the basis of the results so far the effects of demineralization and acid-catalyzed cross-linking of the coal structure are not separated. These results will be investigated further.

3. CHARACTERIZATION OF COAL LIQUIDS

A. INTRODUCTION

The characterization of the soluble material derived from the coals is a significant goal of this project. In Phase I of the project procedures for the characterization were to be established and preliminary work begun. The analysis of the coal liquids derived from the clathrate process presents new applications of existing methods since the thermolysis history of high temperature hydroliquefaction samples is absent. Preliminary data on the products obtained with variation of the nature of the coal, time and extraction procedure, have been obtained. Variations in the material with these parameters and with other factors, such as presence of hydrogen, presence of catalyst, variation in temperature, will be investigated in detail in the next phase of the project. Preliminary data show variations in the aromatic/aliphatic ratio of the toluene soluble material with time and with the nature of the extraction process (see Sections II.1.B.b.i and II.1.B.d.ii.) and major differences between the volatile components derived from the clathrate process and simple solvent extraction (see Section II.3.B.3.).

The majority of the characterization studies have been (and continue to be) carried out on material derived from the batch extraction procedure (Appendix II.1.4.). This procedure yields five groups (fractions) of soluble material: (i) toluene solubles; (ii) and (iii) chloroform solubles derived from the coal and clathrate phases; (iv) and (v) pyridine solubles derived from the coal and clathrate residues. The analytical approach to be employed in Phase II of the project, for the characterization and comparison of each of the materials, has been described in Phase II of the proposal (DSS Z5ST-23440-2-9100) and is summarized, in chart form in Appendix II.3.1.

Procedures have been developed for the examination of the materials by infra-red spectroscopy (Appendices II.3.2 and II.3.3), gas chromatography (Appendices II.3.4, II.3.5 and II.3.6), GC/mass spectrometry (Appendices II.3.7 and II.3.8), and nuclear magnetic resonance spectroscopy (Appendices II.7.9 and II.3.10) and vapour phase osmometry (Appendices II.3.11 and II.3.12). Liquid chromatographic procedures are being developed (see II.3.B.d) as are modifications to the other existing procedures as such modifications are needed (see the following sections). The techniques which have been developed have been applied to selected samples as discussed below and elsewhere in this report.

B. RESULTS AND DISCUSSION

a) Infra-red Spectroscopy

Infra-red (IR) spectra of the hydrocarbon materials derived from batch extraction trials (Appendix II.1.4) with K-seam, Devco, Merritt, Telkwa, Mary Lee and Quinsam coals have been recorded. As indicated in Table 3.1 the IR spectra of the toluene and both chloroform soluble fractions have been obtained. Representative spectra are presented in Appendix II.3.13. The spectra were recorded as solutions in either trichloroethylene or chloroform-d (see Appendices II.3.2 and II.3.3).

The IR spectra of the three fractions (toluene and chloroform solubles) are very similar for each of the coals, as are the spectra of

Table 3.1. List of samples on which infra-red spectra were recorded.

Experiment		Fraction		
No.	Description	Toluene Solubles	$CHCl_3$ Extract of Clathrate Residue	$CHCl_3$ Extract of Coal Residue
2-9	K, clathrate, sequential	x	*	*
2-11	K, clathrate, sequential	x	*	*
2-12	K, clathrate, sequential	x	*	*
2-14	K, clathrate, sequential	x	*	*
2-28	K, clathrate, 20 hrs continous	x	x	x
2-30	K, clathrate, 4 hrs continuous	x	x	x
2-31	K, clathrate $[Fe(C_5H_5)(arene)]^+$ H_2, 4 hrs	x	x	x
2-32	K, clathrate, $Fe(CO)_5$, H_2, 4 hrs	x	x	x
2-33	Coal residue from #2-32, clathrate, 20 hrs	x	x	x
6-2	Telkwa, clathrate, sequential	x	*	*
7-2	Merritt, clathrate, sequential	x	*	*
10-4	Devco, clathrate, $Mn(C_5H_5)(CO)_3$, H_2, 4 hrs	x	x	x
10-7	Devco, clathrate, 20 hrs	x	x	x
10-11	Devco, clathrate, 4 hrs	x	x	x
10-12	Devco, clathrate, $[(arene)-Mn(CO)_3]^+$, H_2, 20 hrs	x	x	x
11-2-1	Pyridine extracted K coal, clathrate, 20 hrs	x	x	x
11-10-1	Devco, clathrate, H_2, 4 hrs	x	x	x
11-10-4	Devco, clathrate, H_2, 20 hrs	x	x	x
13-1	Quinsam, 20 hrs	x	x	x
14-1	Mary Lee, clathrate, 20 hrs	x	x	x

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*Experiment workup procedure used at this time (Appendix II.1.2.b) did not yield $CHCl_3$ extract of this fraction. The infra-red spectrum of the toluene extract of this fraction was recorded in its place.

the materials derived from the trials with different coals (Appendix II.3.13). Interpretation of these data will be carried out in conjunction with the data obtained on the same samples by the other techniques described in this section.

The IR spectra of the pyridine soluble materials will be recorded after the optimisation of the procedure for the removal of pyridine contamination of the samples (Appendix II.1.9). These materials will be examined as KBr pellets or fluorolube mulls. The IR data will yield valuable information concerning the nature of the pyridine soluble materials (see for example Drake and Jones, 1983).

b) Nuclear Magnetic Resonance Spectroscopy

Proton nuclear magnetic resonance (^{1}H NMR) spectra of the hydrocarbon materials derived from experiments with the K-seam, Devco, Quinsam and Mary Lee coals have been recorded by the procedures outlined in Appendices II.3.9 and II.3.10. As indicated in Table 3.2, the ^{1}H NMR spectra of the toluene and both chloroform fractions from selected trials with each of these coals have been obtained as chloroform-d solutions.

The ratio of aromatic to aliphatic protons in each sample may be derived from the NMR spectra. These data (for the toluene soluble material) have been discussed for the sequential extraction procedure elsewhere in this report (Section II.1.B.b.i).

Typical ^{1}H NMR spectra of clathrate-produced hydrocarbons are shown in Appendix II.1.8. These spectra closely resemble ^{1}H NMR spectra of coal liquids produced by more traditional methods (Dickinson, 1980). Information regarding the aromatic content of the hydrocarbon is obtained

Table 3.2. List of samples on which ^1H nuclear magnetic resonance spectra were recorded.

Experiment		Fraction		
No.	Description	Toluene Solubles	$CHCl_3$ Extract of Clathrate Residue	$CHCl_3$ Extract of Coal Residue
2-9	K, clathrate, sequential	x	*	*
2-11	K, clathrate, sequential	x	*	*
2-12	K, clathrate, sequential	x	*	*
2-14	K, clathrate, sequential	x	*	*
2-28	K, clathrate, 20 hrs continuous	x	x	x
2-30	K, clathrate, 4 hrs continuous	x	x	x
2-31	K, clathrate, $[Fe(C_5H_5)(arene)]^+$ H_2, 4 hrs	x	x	x
2-32	K, clathrate, $Fe(CO)_5$, H_2, 4 hrs	x	x	x
2-33	Coal residue from #2-32, clathrate, 20 hrs	x	x	x
2-34	K, clathrate, 20 hrs	x	x	x
2-35	K, clathrate, ferrocene, H_2, 4 hrs	x	x	x
6-2	Telkwa, clathrate, sequential	x	*	*
7-2	Merritt, clathrate, sequential	x	*	*
10-3	Devco, clathrate, $Mn(C_5H_5)(CO)_3$ H_2, 4 hrs	x	x	x
10-4	Devco, clathrate, $Mn(C_5H_5)(CO)_3$ H_2, 4 hrs	x	x	x
10-12	Devco, clathrate, $Mn(C_5H_5)(CO)_3$, H_2, 20 hrs	x	x	x
11-10-1	Devco, clathrate, H_2, 4 hrs	x	x	x
11-10-3	Devco, toluene + pyridine, 18 hr soxhlets	x		
11-10-4	Devco, clathrate, H_2, 20 hrs	x	x	x
11-2-1	Pyridine extracted K coal, clathrate, 20 hrs	x	x	x
11-2-2	K, clathrate, H_2, 4 hrs	x	x	x
13-1	Quinsam, clathrate, 20 hrs	x	x	x
13-2	Quinsam, clathrate, 20 hrs	x	x	x
14-2	Mary Lee, clathrate, 20 hrs	x	x	x

Table 3.2. continued

*Experiment workup procedure used at this time (Appendix II.1.2.b) did not yield $CHCl_3$ extract of this fraction. The NMR spectrum of the toluene extract of this fraction was recorded in its place.

from the 5.5 - 9.0 ppm chemical shift range; the 0.5 - 5.5 ppm region shows some details of the aliphatic region. Three distinct resonance regions are apparent in the aliphatic region of this spectrum. The resonances in the 0.5 - 1.0 ppm region are assigned to methyl protons γ or further from an aromatic ring; the 1.0 - 1.6 ppm region to methylene protons β or further from the ring and to methyl protons β to the ring; and the 2.0 - 3.3 ppm region to protons on carbon atoms α to the ring (Bartle and Jones, 1978). Two other aliphatic ranges, less distinct in the spectrum shown, are the 1.6 - 2.0 ppm region (assigned to naphthenic methylene and methine, other than α to the ring) and the 3.3 - 4.5 ppm region (assigned to methylene groups which are α to two rings).

The ^1H NMR (250 MHz) spectra of four of the hydrocarbon materials obtained from Experiment 2-30, a continuous clathrate extraction of K-seam coal (described in Appendix II.1.5), are shown in Appendix II.1.13. The spectra are for material from the toluene layer in contact with the clathrate, the toluene in the reflux vessel, and chloroform extracts of the coal and clathrate. The differences in the aromatic/aliphatic ratios have been discussed in Section II.1.B.d.ii, but a more detailed interpretation of the spectra is of interest. In particular, the difference in aromatic/aliphatic proton ratio between the two toluene soluble fractions is very pronounced. The aromatic/aliphatic ratio is much larger for the toluene soluble material (Figure 1 of Appendix II.1.13) that collected in the reflux flask as the experiment progressed, than for the toluene soluble material (Figure 2 of Appendix II.1.13) that was in contact with the coal and clathrate phases at the end of the experiment. The changes in the intensity of the 2.0 - 3.3 ppm region are consistent with the changes in the aromatic (5.5 - 9.0 ppm) region as these resonances are attributed to protons on carbon atoms α to the aromatic ring. The ^1H NMR spectra of the four hydrocarbon materials produced in experiment 2-28 (also a continuous extraction of K-seam coal) follow the same trend as observed in the experiment 2-30 spectra shown.

Satisfactory NMR spectra have not yet been obtained on the pyridine soluble material because of interference in the aromatic region by residual pyridine in the samples. Once the pyridine removal technique has been optimized (see Appendix II.1.9) these materials will be investigated further.

The ^{13}C NMR spectra of three clathrate produced hydrocarbons from K-seam coal are shown in Appendix II.3.14. These spectra indicate qualitative differences between the samples examined and suggest that this technique will be useful for studying clathrate produced hydrocarbons. However further work is required before they may be used to determine the aromaticity of the material as relaxation agents must be tested (Bartle and Jones, 1978).

c) Molecular Weight by Vapour Phase Osmometry

The number average molecular weights of the hydrocarbon materials derived from experiments with K-seam and Devco coal are being determined by vapour phase osmometry (VPO) using a Hitachi-Perkin Elmer Molecular Weight Apparatus. Details of the procedure are given in Appendices II.3.11 and II.3.12. Preliminary data obtained to date are listed in Table 3.3. The toluene soluble fraction and the chloroform extracts of the clathrate and coal residues were analyzed as dilute solutions in benzene. The

Table 3.3. Molecular weight data obtained by Vapour Phase Osmometry.

Experiment		Molecular Weight		
No.	Description	Toluene Soluble Fraction	$CHCl_3$ Extract of Clathrate Residue	$CHCl_3$ Extract of Coal Residue
2-21#3	K_B coal, clathrate 16 hrs	421	489	498
2-40	K_B coal, clathrate 4 hrs	449, 420	492	480
11-2-2	K_B coal, clathrate hydrogenated, 4 hrs	463	458	488
10-11	Devco, clathrate 4 hrs	516	492	446
11-10-1	Devco, Pr_4N clathrate hydrogenated, 4 hrs	412	439	452

molecular weights of these three hydrocarbon fractions are very similar and further data, with a revised procedure, are required prior to reaching any conclusions. The data obtained will be used to compare the clathrate-produced liquids from each of the coals with the high-temperature liquids (obtained from B.C. Research) and with the liquids obtained by solvent extractions of the coals. The molecular weights of the three toluene soluble fractions obtained from each coal/clathrate experiment will also be examined as a function of liquefaction conditions (time, temperature, H_2, catalyst, etc.).

The molecular weight of the pyridine soluble materials from the coal/clathrate experiment will be determined in a similar fashion. The molecular weight of the whole pyridine soluble material is of interest, but the method will also be used in conjunction with the gel permeation chromatographic (GPC) fractionation of the pyridine soluble material as outlined in Appendix II.3.1.

d) Liquid Chromatography

High performance liquid chromatographic (HPLC) techniques for the fractionation of the coal liquids on either a class separation basis, or a molecular size basis as outlined in Appendix II.3.1, are in the early stages of development. Class separation is being achieved through the use of a silica HPLC column (Water μ Porasil) and hexane/methylene chloride solvents by adaption of the method of Suantoni and Swab (1975). Class separation methods using RNH_2 and C_{18} columns will also be examined for application to the clathrate produced coal liquids. Preparative scale molecular size fractionation is being attempted by use of a Sephadex LH-20 gel permeation chromatography (GPC) column employing pyridine as the solvent (Schanne and Haenel, 1981). The results of the VPO molecular weight determinations will be used to refine the GPC fractionation procedure. It may be necessary to modify the procedure by using other GPC materials which permit separation of higher molecular weight material than can be achieved with the Sephadex. Styragel (Waters) GPC columns will be used for the analytical scale molecular size determinations of the fractions obtained from the preparative scale GPC column.

e) Gas Chromatography and Gas Chromatography/Mass Spectrometry

Gas chromatographic (GC) analysis of the GC volatile components of material derived from experiments with the K-seam coal have been carried out using a 30m x 0.22 mm ID fused silica capillary column with SE-54 as the active phase. Details of the GC conditions are given in Appendices II.3.5 and II.3.6. A direct on-column injection technique was developed and used to avoid pyrolysis of samples within the inlet. As indicated in Table 3.4 the toluene solubles, the chloroform extracts of the clathrate residues and the chloroform extracts of the coal residues have been analyzed as have toluene extracts of the untreated coal. Representative chromatograms are shown in Appendix II.3.15. The fraction of the material which is GC volatile has been estimated by a simulated distillation procedure to be 15% for the toluene soluble material. Comparisons with the chloroform extracts of the clathrate residues and of the coal residues indicate that approximately 15% and 1 % of each is GC volatile.

Table 3.4. List of samples on which gas chromatograms were recorded.

Sample No.	Description	
	Fraction	Experiment
2-18A	toluene solubles	K, clathrate, sequential
2-21-1A	toluene solubles	K, clathrate, 18 hrs
2-21-4A	toluene solubles	K, clathrate, 18 hrs
2-21-4B	$CHCl_3$ extract of coal residue	K, clathrate, 18 hrs
2-21-4C	$CHCl_3$ extract of clathrate residue	K, clathrate, 18 hrs
2-34A	toluene solubles	K, clathrate, 20 hrs
6-2A	toluene solubles	Telkwa, clathrate, sequential extraction
7-2A	toluene solubles	Merritt, clathrate, sequential extraction
--	toluene solubles	K, soxhlet, 18 hrs
0-20	toluene solubles	Merritt, soxhlet 18 hrs
0-22	toluene solubles	Telkwa, soxhlet 18 hrs

The chromatographs derived from the three types of samples clearly indicate that in each case the composition of the GC volatile material is qualitatively the same, and different to that of the toluene extract of the untreated coal (Appendix II.3.15, Figures 1, 2, 3, 4). With this knowledge a procedure was developed for the removal of much of the non-volatile material without affecting the GC volatile components. The procedure is described in detail in Appendix II.3.4 and consists of a simple separation carried out on a silica Sep-Pak with the elution of the GC volatile material by 25% methylene chloride in hexane. This step in the procedure prevents contamination of the columns in both the GC and GC/MS work, by involatile components.

Gas chromatography/mass spectrometry (GC/MS) of the samples has been conducted to attempt to identify the chemical composition of the components in the GC volatile fraction. The GC/MS analysis was carried out on a Finnigan 3300 GC/MS equipped with a SE-54 fused silica capillary column and coupled to a PDP11/23 based data system (details are given in Appendices II.3.7 and II.3.8). Both chemical and electron impact ionisation spectra were recorded and are in the process of being analyzed. The identities of several specific components are given in Table 3.5. These identifications are based on GC retention index and the mass spectra of comparison compounds in the library in the data system. Identification of other components requires detailed comparison of mass spectra with reference spectra (NIH/EPA Library) and such analysis is in progress.

Further work is in progress on the analysis by GC and GC/MS of these samples and those derived from the Devco coal. A detailed comparison with the direct toluene extraction of the coals is in progress.

Table 3.5. Specific components identified by GC/MS

Sample 2-21-4A[1]	Sample 2-21-4C[2]
Tetralin	Naphthalene *
Naphthalene*	2-Methylnaphthalene
2-Methylnaphthalene	1-Methylnaphthalene
1-Methylnaphthalene	Biphenyl
Biphenyl	2,6-Dimethylnaphthalene
2-Ethylnaphthalene	2,7-Dimethylnaphthalene
1-Ethylnaphthalene	1,3-Dimethylnaphthalene
2,6-Dimethylnaphthalene	1,7-Dimethylnaphthalene
2,7-Dimethylnaphthalene	1,6-Dimethylnaphthalene
1,3-Dimethylnaphthalene	2,3-Dimethylnaphthalene
1,7-Dimethylnaphthalene	1,4-Dimethylnaphthalene
1,6-Dimethylnaphthalene	2,2'-Bipyridyl
2,3-Dimethylnaphthalene	1,2-Dimethylnaphthalene
1,4-Dimethylnaphthalene	Dibenzofuran
1,5-Dimethylnaphthalene	2,3,5-Trimethylnaphthalene
2,2'-Bipyridyl	4,4'-Dimethylbiphenyl
1,2-Dimethylnaphthalene	2-Methylfluorene
Dibenzofuran	1-Methylfluorene
2,3,6-Trimethylnaphthalene	Phenanthrene*
2,3,5-Trimethylnaphthalene	Anthracene*
3,3'-Dimethylbiphenyl	3-Methylphenanthrene
4,4'-Dimethylbiphenyl	3-Methylphenanthrene
2-Methylfluorene	2-Methylphenanthrene
1-Methylfluorene	9-Methylphenanthrene
Phenanthrene	4-Methylphenanthrene
Anthracene	1-Methylanthracene
3-Methylphenanthrene	1-Methylanthracene
2-Methylphenanthrene	1-Methylphenanthrene
9-Methylphenanthrene	2,7-Dimethylphenanthrene
4-Methylphenanthrene	Benzo[a]fluorene
1-Methylanthracene	Chrysene*
1-Methylphenanthrene	Triphenylene
2,7-Dimethylphenanthrene	
Chrysene*	

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[1] Toluene soluble fraction of K coal/clathrate extraction.

[2] $CHCl_3$ extraction of clathrate residue of a K coal/clathrate extraction.

*Added as internal standard.

Trials with samples from catalytic upgrading with clathrate (Section II.4) are also being conducted. Comparison with the products of high temperature liquefaction of K-seam and Devco coals will also be undertaken.

4. CATALYTIC HYDROGENATION ('UPGRADING')

A. INTRODUCTION

To address the problem of increasing the hydrogen content of solubilized coal-derived material, incorporation of a hydrogenation catalyst into the medium under investigation (clathrate) has been put forward as a vital element of the overall programme. While this area was originally (1981) proposed as a major theme for Phase II, with the agreement of the Scientific Authority preliminary (feasibility) studies have been conducted during Phase I, in relation to a number of directions as described below. The information provided by these introductory experiments will provide a framework in which to plan the development of novel upgrading techniques which are to be addressed as a major objective of Phase II.

Possible methodology for promoting catalytic hydrogenation in the clathrate medium may rely on several inter-related approaches which include: (a) Use of a clathrating substrate able to effect hydrogenation or hydrogenolysis, which would lead to an immobilized homogeneous catalytic component; (b) Application of a clathrate-miscible homogeneous hydrogenation catalyst; (c) Addition to the medium of a conventional heterogeneous hydrogenation catalyst; (d) Utilization of autocatalytic properties accruing from mineral content of the coal mass. Of these avenues only (b) has been previously examined, by the Alabama group leading to qualitative evidence for enhancement of coal solubilization in the presence of added hydrogen gas. A major obstacle to structured research into this aspect of clathrate behaviour is the very limited information available concerning solvent properties of the clathrate phase in relation to a variety of relevant substrates. Research within category (a) above is contingent on fabrication of a stable clathrate derived from an ionic component having established hydrogenation capability while progress within category (d) relies in the first instance on advancement *via* fortuitous results, with subsequent attempts at rationalization.

B. RESULTS AND DISCUSSION

a) Catalyst as Clathrate Constituent

Previous work conducted by the Alabama group has shown that the iodide salt of the $Cr(C_6H_6)_2^+$ cation will form a typical liquid clathrate in the presence of aromatic liquids and $AlMe_3$, although the properties of the resulting system have yet to be investigated. Development of this observation at the University of Victoria (NSERC-funded research) has shown that it is possible to generate stable clathrates using other cationic salts including $[Fe(C_5H_5)(arene)]PF_6$ and $[Mn(CO)_3(arene)]PF_6$, from which addition of toluene and $AlEt_3$ leads to formation of highly coloured two-phase systems (Appendix II.4.1). It has since been found that these new clathrate phases are completely miscible with the $AlEt_3/Pr_4NI$ systems which we have been using in our investigation of the effect on coal solubilization of the clathrate phenomenon. Extrapolation of these facts to the present contract project indicates that it will indeed be possible during Phase II to examine the influence on coal extraction yields of incorporation into the clathrate phase of transition-metal components with potential for *in situ* upgrading.

b) Homogeneous Catalysis

Previous work conducted by the Alabama group has also indicated that there is a significant enhancement of liquid yield from coal on addition of arene-chromium or -manganese carbonyl derivatives [specifically $Cr(arene)(CO)_3$ or $Mn(C_5H_5(CO)_3]$ in the presence of hydrogen gas. Trial experiments directed towards confirming such observations provide support for an effect on overall yield and also on distribution of solubles among the solvents used for recovery of solubilized material. Preliminary results are set out in Table 4.1. In addition to the $Mn(C_5H_5)(CO)_3$ complex used previously by Atwood we have briefly examined the usefulness of $Fe(CO)_5$, $Cr(C_6H_3Me_3)(CO)_3$, and $Fe(C_5H_5)_2$ as additives. In all cases an increase in solubilization is indicated although insufficient data are yet available to establish meaningful trends. Interpretation of the solubility characteristics of dissolved coal-derived material is complicated by the distribution into the recovery solvents of the neutral transition-metal additives. However it is clear that the latter can enhance toluene and chloroform solubility in the presence of added H_2 and in particular a spectacular increase in overall yield from the Devco coal occurs with the manganese complex. Development of these preliminary observations constitutes a major theme in Phase II.

c) Heterogeneous Catalysis

A single trial experiment has been conducted using pellet form cobalt molybdate catalyst (American Cyanamid, HDS-1442A). The distribution of solubilized material throughout the solvent fractions did not appear to be altered when compared with routine extraction experiments.

d) Heterogeneous:Autocatalytic

The unexpectedly high degree of solubilization of Devco coal following contact with the clathrate medium, together with considerations based on rank and origin of this coal type, led us to speculate that mineral matter present in the coal mass might be responsible for enhancement of liquid yield and that this might be a transferable effect to other coals. To test this possibility several experiments were conducted using mixtures of Devco and K-seam coals. The preliminary results (Table 4.2) suggest that addition of Devco to K-seam coal does enhance the dissolution behaviour of the latter, giving a pattern which may be indicative of autocatalytic properties associated with the Devco material. While the origin of the effect will be necessarily difficult to identify, observations of this kind are important in searching for more effective liquefaction and will be pursued in such a context.

Table 4.1. Effect of transition-metal additives on coal liquid yields obtained from standard 10 g coal samples.

Coal-type	Conditions[a]	Toluene Solubles (g)	Chloroform Solubles (B) (g)	Chloroform Solubles (C) (g)	Pyridine Solubles (g)	Total Solubles (g)	Corrected Solubles[b] (g)
K-seam	No catalyst, no H_2	0.015	0.008	0.035	1.089	1.147	1.147
K-seam	2 g #1, no H_2 [c]	0.549	0.056	0.641	0.915	2.161	1.234
K-seam	2 g #1, H_2 [c]	0.790	0.078	0.787	1.102	2.757	1.830
K-seam	2 ml #2[d]	0.053	0.028	0.142	0.940	1.164	1.164[e]
K-seam	2 g #3 [f]	0.972	0.078	0.863	0.898	2.811	--
K-seam	2 g #4 [g]	0.423	0.106	1.341	0.904	2.774	--
Devco	No catalyst, no H_2	0.048	0.023	0.077	1.629	1.777	1.777
Devco	2 g #1, H_2[c]	0.904	0.148	1.090	3.321	5.423	4.496
Control (no coal)	2 g #1, H_2[c]	0.308	--	0.619	--	0.927	0.000

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[a] all runs conducted for 4 hr at 70°C

[b] corrected for $(C_5H_5)Mn(CO)_3$ as extracted in control

[c] #1 = $(C_5H_5)Mn(CO)_3$

[d] #2 = $Fe(CO)_5$

[e] assuming all $Fe(CO)_5$ removed

[f] #3 = (mesitylene)$Cr(CO)_3$

[g] #4 = ferrocene

Table 4.2. Heterogeneous additive effect on coal liquid yields.[a]

Devco %	K-seam %	# Runs	Toluene Yield (g)	Chloroform Yield (g)	Pyridine Yield (g)	Total Yield (g)	K-extracted[b] (corrected) (g)
0	100	5	0.126	0.165	1.972	2.263	2.263
10	90	2	0.091	0.179	2.394	2.664	2.603
20	80	2	0.118	0.156	2.671	2.745	2.878
50	50	2	0.097	0.201	3.010	3.308	3.400
100	0	3	0.117	0.204	2.894	3.215	--
0	100[c]	1	0.074	0.163	2.116	2.353	2.353

---

[a] all runs conducted at 70° for 20 hr. 10 g coal used in each case. No H_2.

[b] assuming same relative percentage of Devco extracted.

[c] 1.05 g catalyst (COMo) used. H_2 1 atm.

III. INTERIM CONCLUSIONS AND PROJECTIONS

1. The effective dissolution of bituminous Canadian coals at 70°C and one atmosphere employing a two-phase liquid clathrate-toluene solvent system has been demonstrated, using principally the salt tetrapropylammonium triethylaluminum iodide as the clathrating agent.
2. The yield of liquid product, ex pyridine insolubles, for an Eastern marine coal, Devco Cape Breton was 32 ± 2 per cent, and for an A bituminous Cretaceous coal (Fording Mines, British Columbia, 22 ± 2 per cent in the absence of catalytic upgrading or an active donor solvent. In contrast, the direct pyridine (soxhlet) solubility of the same coals was 8.9 and 9.5 per cent respectively. Characteristic yields < 1% were obtained with toluene alone.
3. The dissolution was shown to be principally physical in nature, mainly dependent on the ionic atmosphere of the novel liquid clathrate phase. Accordingly, the yield from low ranked but reactive Western coals (in terms of oxygen functionalities) such as oxidized Hat Creek and Forestburg sub-bituminous coals were negligible in the absence of upgrading. Reduced yields from intermediate rank coals (Qunisam and Telkwa) were observed. Significantly, the clathrate phase showed long term stability (months) in the presence of low rank coals, providing further confirmation of a purely medium effect.
4. In this initial development phase of the clathrate salt novel technology, the following basic procedures have been established:
    (a) *Synthesis and manipulation* of clathrating salts including examples incorporating potentially promising cationic hydrogenation catalysts.

(b) *Non-destructive workup methods* allowing solvent partition (toluene, chloroform and pyridine) for comparison with high temperature technologies.

(c) *Gravimetric assays* including reproducibility and mass balance studies to ensure elimination of (clathrating) salt entrainment while subjecting the hydrocarbon product to a minimum of re-polymerization. Further work on these methods is in progress.

5. A range of conditions has been applied in the clathrate extraction in a programme designed to optimize yields (item 2) *viz.*

(i) length of extraction time

(ii) clathrate/coal ratio

(iii) continuous, batch and sequential experiments with respect to toluene stripping solvent

(iv) coal quality: effects of air oxidation and demineralization (acid treatment) on yields

(v) effect of sequential clathrate treatment.

It has been observed that sequential clathrate treatment raised the yield to 50% overall in two passes (Devco). Work is in progress in this area.

While acid treatment reduced yield, air oxidation did not appear to be a significant negative factor in the extraction.

6. Exploratory work has been carried out on catalytic upgrading with experimental parameters as follows:

(i) homogeneous catalysts (locked in)

example $(Ar)(Cp)Fe^{+}Al(Et)_3PF_6^{-}$

(ii) homogeneous catalyst (neutral)

example $(C_5H_5)Mn(CO)_3$

(iii) heterogeneous catalyst

example CoMo (commercial, not directly presulphided)

(iv) potential autocatalysis

example Devco + K-seam co-dissolution as a function of relative percentage Devco

All experiments are under continuous bubbling with dry hydrogen at one atmosphere.

Results to date have been indicative of potential success in upgrading. For example, toluene solubles and the aliphatic/aromatic ratio (factors suggestive of net upgrading) both increased for the homogeneous catalysts (locked in and neutral); and there was an indication of increased yield for the neutral manganese catalyst plus hydrogen. Though the conventional CoMo catalyst gave no improvement in yield, the initial data on co-dissolution of K-seam and Devco showed autocatalytic potential. Activity of reduced iron sulphides, known to be active in solvent refined coal processes, is suspected.

7. Analytical and spectroscopic procedures for the analysis of the coal products were to be established in the initial phase. This development programme has been completed in the following areas: Infra-red, ^{1}H NMR, ^{13}C NMR, solvent partition, elemental analysis, molecular weight (osmometry), residue on ignition (ash), GC, GC/MS. Additionally, GPC and HPLC methods are under development at this time.

Preliminary results of ^{1}H NMR studies have provided useful information on (i) sequence of extraction of aliphatic and aromatic components, (ii) potential contamination of the clathrate layer, (iii) changes in catalyst structure during extraction, and (iv) course of continuous extraction.

GC/MS studies on fractions from direct solvent extraction and clathrate runs provide a contrast and comparison of the low molecular weight hydrocarbon components.

Further work on coal structure via spectroscopic information and chromatographic separation is in progress.

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APPENDIX I.1.1

INTRODUCTION TO LIQUID CLATHRATE BEHAVIOUR

INTRODUCTION TO LIQUID CLATHRATE BEHAVIOUR

The term clathrate is used to define that class of substances formed from two different stable compounds without the existence of a chemical bond between them. This behaviour is normally found when one compound (the host) crystallizes, because of its shape, in a fashion such that there exist cavities or holes in the lattice. The second compound (the guest) can then be trapped in these cavities. Although the original use of the term was restricted to solids, Atwood reported in 1974 a group of compounds which exhibit properties in the liquid state strongly reminiscent of clathrates. The term "liquid clathrate" was therefore used to describe the new substances. In order to appreciate the novelty and indeed the power of liquid clathrates, a few paragraphs must be devoted to the discovery of this phenomenon.

As part of a general study of compounds related to so-called Ziegler-Natta catalysis, Ziegler and co-workers reported in 1960 the synthesis of compounds of the type $M[Al_2R_6X]$ according to Equation (1). Since $M[Al_2R_6X]$ are ionic compounds, all of the initial work on them was done in basic solvents. In early 1970, Atwood attempted to dissolve $K[Al_2Me_6N_3]$ in benzene. Surprisingly the material dissolved quickly, and two liquid layers were observed. The composition of the system is shown schematically in Figure 1. Subsequently the scope of Equation 1 was rapidly expanded and the liquid-layering effect was obtained for virtually all combinations of M, X, and R. An idea of the range of

$$2AlR_3 + MX \rightarrow M[Al_2R_6X] \qquad (1)$$

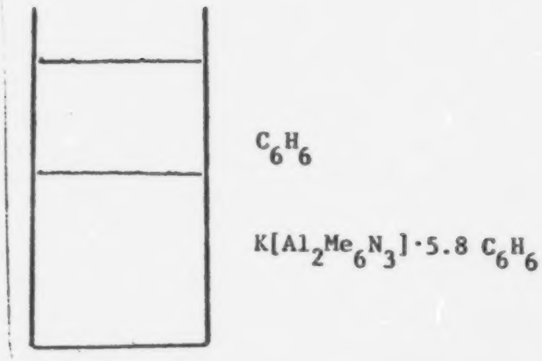

Figure 1.

choices is given in Table 1. In the early 1970's, several observations were made which resulted in the formulation of the theory of liquid clathrates

Table 1. Components of the $M[Al_2R_6X]$ Parent Compound

M	R	X
Na^+	$-CH_3$	F^-
K^+	$-C_2H_5$	Cl^-
Rb^+	$-C_3H_7$	Br^-
Cs^+	$-C_4H_9$	I^-
NR_4^+		N_3^-
PR_4^+		SCN^-
$(C_6H_6)_2Cr^+$		$SeCN^-$
$(C_5H_5)_2Co^+$		NO_3^-
Ba^{2+}		CH_3COO^-
		$HCOO^-$
		NO_2^-
		O_2^-
		OH^-
		SO_4^{2-}
		CO_3^{2-}
		O^{2-}

(and in fact, the name itself). The most important of these are given in the following:

(a) The behaviour is observed only in aromatic solvents. Aliphatic compounds such as hexane or cyclohexane do not dissolve the "parent compounds", $M[Al_2R_6X]$, and ethers or amines do not produce the two-layer situation.

(b) All of the parent compound is confined to the lower layer. The upper one contains only the excess aromatic.

(c) For a given set of M, X, R, and aromatic the lower layer will only load a given amount of aromatic. This is referred to as the A/A (aromatic-to-anion) ratio, and it is a constant, provided enough aromatic is present.

(d) For a given set of X, R, and aromatic the A/A ratio increases as M increases in size. For example, the compositions are $K[Al_2Me_6N_3]\cdot 5.8\ C_6H_6$ *vs.* $Cs[Al_2Me_6N_3]\cdot 7.4\ C_6H_6$ and $[NMe_4][Al_2Me_6I]\cdot 5.0\ C_6H_5Me$ *vs.* $[NBu_4][Al_2Me_6I]\cdot 7.0\ C_6H_5Me$.

(e) For a given set of M, X, and aromatic, the A/A ratio increases as R increases in length (this is, in essence, an increase in the size of the anion). For example, the compositions are $[NMe_4]$-$[Al_2Me_6I]\cdot 5.0\ C_6H_5Me$ *vs.* $[NMe_4][Al_2Et_6I]\cdot 12.9\ C_6H_5Me$.

(f) For a given set of M, X, and R the A/A ratio decreases as the aromatic increases in size. For example, $K[Al_2Me_6N_3]\cdot 5.8\ C_6H_6$ *vs.* $K[Al_2Me_6N_3]\cdot 3.8\ C_6H_5Me$.

(g) The aromatic is trapped by, not bonded to the parent compound, and may be freed in some cases by a small change in temperature. For example the equilibrium shown in Equation (2) pertains.

$$K[Al_2Me_6N_3] + 5.8\ C_6H_6 \rightleftharpoons K[Al_2Me_6N_3]\cdot 5.8\ C_6H_6 \qquad (2)$$

L.T. liquid clathrate

The above observations are quite general; approximately 1,000 different combinations of M, X, R, and aromatic have been examined. The last four observations, (d), (e), (f) and (g) are consistent with a situation in which the lower liquid layer behaves in a manner analogous to that of a solid-state clathrate. In the liquid clathrate the parent compound functions as the host, and the aromatic, the guest.

Of the compounds discussed thus far, all are oxygen- and water-sensitive materials. However, the reactivity of the parent compounds is, in general, much less than that of the aluminum alkyls themselves.

A rather complicated theory has been developed to explain the novel behaviour of ionic compounds in non-polar solvents, but the current view may be summarized with regard to three points: (1) The parent compound must intrinsically possess a low lattice energy. (2) The anion and the cation of the parent compound must be capable of a strong interaction with each other. (3) Attention must be focussed on the role of the relative sizes of the cation and anion, even in situations where both (1) and (2) are operative. Conditions (1) and (2) are usually met for $M[Al_2R_6X]$ which possesses an angular structure as shown in Figure 2. If the anion is represented as "Y" and the aromatic as "|" in two dimensions, then the liquid clathrate structure may be viewed as in Figure 3.

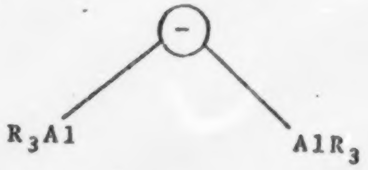

Figure 2.

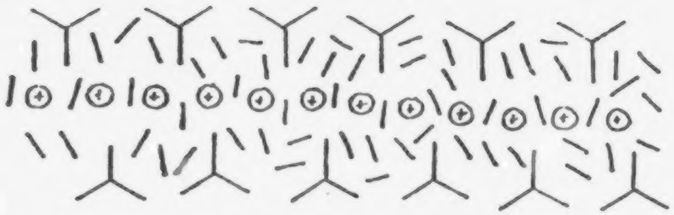

Figure 3.

Such a model is consistent with the observed data, and it carries predictive power. The view is that the liquid clathrate is maintained by a cooperative effect, and originates with a "Y" shape for the anion.

The true test of the theory lies in the ability to predict the existence of new liquid clathrates composed of completely different chemical substances. The anion shown in Figure 2 is geometrically related to that of the hexamethyldisilazane anion, Figure 4. One would therefore predict

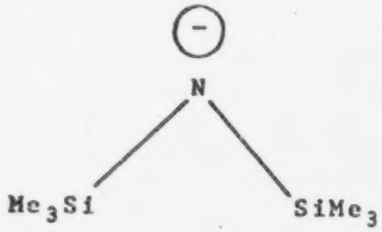

Figure 4.

that $Na[N(SiMe_3)_2]$, or equivalently $Na[Si_2Me_6N]$, should exhibit liquid clathrate behaviour. In fact, $Na[N(SiMe_3)_2]$ dissolves directly in an aromatic solvent to give a true solution. The understanding of this lies in a consideration of the size of the Na^+ ion compared to that of the anion. In solution, discrete dimers are formed, and a cooperative interaction as needed for liquid clathrate formation cannot occur. However, if one effectively makes the cation larger by complcxation with a crown ether such as 15-crown-5 (Figure 5), the dimer is not able to form, a long-range cooperative interaction is forced upon the system, and a liquid clathrate is obtained. The liquid clathrates based on $M[Si_2Me_6X]$ do not differ significantly from those derived from $M[Al_2Me_6X]$. These observations are of critical importance in that they demonstrate the generality of liquid clathrate behaviour.

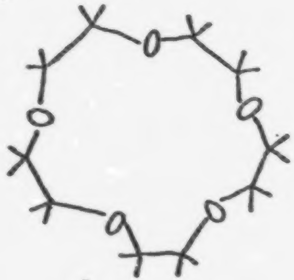

Figure 5.

The liquid clathrates have been extensively investigated with regard to their ability to perform separations, and they also act as heat transfer media. However, their greatest potential lies in the area of coal dissolution. The novel combination of aromatic content with high ionic strength is believed responsible for the dramatic interaction with coal. This, combined with the liquid-layering effect which makes extraction of products a tractable proposition, forms the basis for the research discussed in this Report. Two reviews of liquid clathrates are available.

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APPENDIX II.1.1

PREPARATION OF LIQUID CLATHRATES

PREPARATION OF LIQUID CLATHRATES

The method outlined was applicable to the series of clathrates based on $[NR_4]$ (Al_2Et_6I) (R=Me, Et, Pr, Bu). The liquid clathrate routinely used for coal extractions was made in about 500 ml batches. 100 g of NPr_4I (0.319 mole) was placed in a 1000 ml Erlenmeyer flask and transferred to the inert atmosphere glove box. 500 ml of distilled toluene (stored over molecular sieves) was poured over the salt and 87 ml (.638 mole) of $AlEt_3$ was slowly added. Following mixing for approximately 5 minutes approximately 500 ml of liquid clathrate formed and all the NPr_4I dissolved. The Erlenmeyer was stoppered and the liquid clathrate stored in the inert atmosphere glove box until needed. The liquid clathrate was stable indefinitely under these conditions. ^1H NMR spectra of the series of clathrates $[NR_4](Al_2Et_6I)\cdot$toluene (R=Me, Et, Pr, Bu) are presented in Figures 1-4, Appendix II.1.10.

APPENDIX II.1.2

METHODS FOR QUENCHING THE COAL/CLATHRATE SYSTEM
AND
SEPARATION OF MATERIALS

a. After January 1984

b. Prior to January 1984

METHODS FOR QUENCHING THE COAL/CLATHRATE SYSTEM
AND
SEPARATION OF MATERIALS

a. After January 1984

The procedures described in Appendix II.1.2.b were not satisfactory as the isolated materials contained excessive inorganic salt contamination. In all cases the material from the extractions consisted of the three phases i.e., toluene, clathrate and coal residue.

(i) Toluene Phase:

The procedure was carried out under a nitrogen stream directed through a large plastic funnel. 20 ml of 10^{-4}M HCl was added to each 50 ml of toluene in the flask. The acid was added slowly until the vigorous reaction ceased; it was then added more rapidly. After at least 15 minutes (all activity ceased) the mixture was filtered through a Buchner funnel.

The filter paper and cake were placed in a 50 ml beaker to dry. The filtrate was poured into a 250 ml separatory funnel (no grease was used). The flask was rinsed with distilled water which was added to the funnel. The aqueous layer was allowed to settle and was drained after which 20 ml of distilled water was added to the toluene. The funnel was shaken (three times with venting) and the water drained. The wash procedure was repeated five times. Bubbles or contaminants which adhered to the sides of the funnel were washed off with distilled water. The toluene was transferred to a distillation flask (tared) and distilled (Appendix II.1.7).

After distillation of the toluene, the flask was dried on the vacuum line for 15 - 30 minutes and then weighed. The contents of the flask were dissolved in chloroform-d and transferred to a 6-dram vial. The sample was frozen in the vial.

The inorganic residue from the acid wash was dried in a vacuum oven at 100°C overnight. The filter cake was allowed to cool in a desicator, transferred to a 2 dram vial and stored.

(ii) Clathrate Phase:

The clathrate layer poured slowly into a beaker which contained 1ℓ of 10% HCℓ mixed with ice. The HCℓ was stirred rapidly during the addition. When the reaction subsided 100 - 200 ml of chloroform was added to dissolve the black organic material. The aqueous layer was decanted and the remainder filtered through a Buchner filter. The residue was transferred to the filter by rinsing with chloroform. The residue cake was washed with 500 ml of 10% HCℓ and chloroform; it was then dried, weighed and retained for pyridine extraction. The chloroform layers were treated as described below.

(iii) Coal Residue Phase:

The coal residue was transferred (using toluene) from the reaction vessel to a beaker containing a 10% HCℓ ice/water solution, with rapid stirring. The residue was treated with chloroform and washed as for the clathrate phase.

The clathrate phase and coal residue treatments resulted in a chloroform solution and a solid residue from each. These were then treated as follows to extract the organic material.

a) Chloroform solutions:

Two x 2ℓ solutions of cold/5% HCℓ were prepared (one for each chloroform fraction). All manipulations were carried out under a flood of nitrogen.

The chloroform/10% HCℓ mixture was placed in a 2ℓ separatory funnel (no grease). The chloroform layer was run into an Erlenmeyer flask (about 800 ml of chloroform from the clathrate phase or 600 ml from the coal residue phase). The acid layer was discarded.

The chloroform solution was placed in a separatory funnel and shaken vigorously with 1ℓ of 5% HCℓ. The shaking was repeated three times, with venting. The layers were allowed to separate and the chloroform layer run off (taking care to exclude solid material). The aqueous layer was descarded, the funnel rinsed and the wash of the chloroform layer with 1ℓ of HCℓ repeated. The chloroform layer was washed twice more with 500 ml portions of distilled water and slowly drained into a dry 1ℓ wide-mouthed Erlenmeyer flask. Anhydrous sodium sulphate was added to cover the bottom of the flask. The flask was stoppered and swirled. The mixture was allowed to settle until no longer cloudy (approximately 10 minutes). The solution was filtered using a Buchner filter and all the sodium sulphate transferred to the funnel and washed with chloroform until the filter cake was white.

The chloroform was transferred with careful rinsing to a round bottom flask. The bulk of the chloroform was removed on a rotovap with a water bath of less than 50°C. When the volume had been reduced to less than 50 ml, it was transferred to a tared round-bottom flask for distillation (Appendix II.1.7).

b. Solid Residues - Cold Pyridine Wash

The coal or clathrate residue was weighed and transferred to a 250 ml Erlenmeyer flask with a stirring bar. Working in a fumehood, 100 ml of dry pyridine was added to the flask and the mixture stirred for 30 minutes.

The contents of the flask were filtered through a Buchner filter using a pre-weighed filter paper. The residue was washed with small amounts of dry pyridine until the filtrate was clear (or very light brown). The filter was left running for a further 30 minutes. The filter cake was dried in a vacuum oven overnight at 80°C and weighed. The filtrate was vacuum distilled (Appendix II.1.7). After vacuum distillation the residue was pumped on a vacuum line until the odour of pyridine was no longer evident. The residue was then weighed and stored.

METHODS FOR QUENCHING THE COAL/CLATHRATE SYSTEM

AND

SEPARATION OF MATERIALS

b. PRIOR TO JANUARY 1984

The reaction mixture contained three phases; *i.e.,* toluene clathrate and coal residue.

(i) Toluene Phase:

All work was conducted under a nitrogen flood. The toluene was washed with 20 ml of 10^{-4}M HCl; the washing was accompanied by deposition of varying amounts of solid. The mixture was filtered through a pre-weighed (dry) filter paper and the filter cake dried in an oven. The filtrate was placed in a separatory funnel and the two layers allowed to form. The aqueous layer was discarded and the toluene layer placed in a round bottom flask for vacuum distillation (Appendix II.1.7). The residue appeared to contain irreproducible amounts of white solid.

(ii) Clathrate Phase and Coal Residue Phase

Water was slowly added to each of the clathrate phase and the coal residue phase, whilst cooling the mixture in an ice bath. Initially the reaction was quite violent and care was required. After the reaction ceased the resultant materials were transferred to soxhlet thimbles and extracted with toluene for 17 hours (overnight). The toluene solubles were vacuum distilled (Appendix II.1.7).

The soxhlet thimbles were allowed to dry for one day, washed with 500 ml of water and dried in a vacuum oven prior to weighing. The thimble and contents were then extracted in a pyridine soxhlet for 17 hours. The pyridine solution was vacuum distilled (Appendix II.1.7) and the residues dried and weighed. The weights of these residues were usually greater than 10g, indicating significant contamination.

APPENDIX II.1.3

SEQUENTIAL EXTRACTION PROCEDURE

SEQUENTIAL EXTRACTION PROCEDURE

The procedure initially adopted to examine the dissolution of the coal was to remove fractions of the toluene layer at specific time intervals. The progress of the dissolution was monitored by the hydrocarbon content of the toluene fractions. Individual trials were conducted over various periods of up to two weeks. The standard procedure was as follows: 10 g of pulverised, vacuum dried coal was weighed into the reaction vessel together with a magnetic stirring bar. The reaction vessel was placed in the inert atmosphere dry box and 100 ml of clathrate was added together with 100 ml of distilled toluene which had been stored over a molecular sieve. After mixing the reagents the vessel was removed from the dry box. A nitrogen atmosphere was maintained in the vessel by attaching the sidearm to a dry nitrogen stream. The reaction vessel was immersed in an oil bath pre-heated to 70^{o} and the stirring action adjusted to give good mixing of the three phases (i.e. a small vortex formed at the top of the toluene layer). The temperature was maintained at 70^{o}C.

At the selected time the mixture was allowed to settle when three layers formed (about 2 minutes). 50 ml of the toluene layer was withdrawn, using a nitrogen-flushed pipette. 50 ml of freshly distilled toluene was added to the reaction vessel and the vessel re-immersed in the oil bath and stirring resumed. The 50 ml toluene extract was placed in a stoppered 150 ml erlenmeyer flask which had been flushed with nitrogen. This flask was kept in an ice bath until the start of the work-up procedure (Appendix II.1.2.b).

At the end of the trial the whole toluene layer was removed. The clathrate layer was poured off from the coal residue into a nitrogen flushed flask, to which water was slowly added until reaction ceased. Water was also slowly added to the coal residue, to quench any clathrate in this fraction. The work-up of each fraction is described in Appendix II.1.2.b.

APPENDIX II.1.4

BATCH EXTRACTION PROCEDURES

BATCH EXTRACTION PROCEDURES

a) Clathrate Only.

10.00 g of the appropriate coal was placed with a magnetic stirrer bar in a 400 ml schenk flask. The flask was introduced into the dry box in the normal manner (see Appendix B for dry box procedure). The desired amount of $(NPr_4)(Al_2Et_6I)$.n-toluene liquid clathrate (100 ml for most extractions) was measured in a measuring cylinder and poured over the coal. With most coals the clathrate darkened immediately but there was no other signs of reaction. 100 ml of toluene (freshly distilled and stored over molecular sieves) was then added. The flask stoppered, and removed from the dry box and placed in fumehood under a constant but slow flow of nitrogen. The flask was maintained at 70^{o} in an oil bath for the desired time (usually either 4 hours or 20 hours) whilst the coal and the two phases were stirred. The mixture was allowed to cool under an excess pressure of nitrogen.

b) Catalyst.

The procedure was as outlined in (a) until addition of the liquid clathrate. At this point the catalyst was introduced. If the catalyst was fully homogeneous and neutral then the desired amount was added before adding 100 ml of the liquid clathrate. If the catalyst was of the transition metal sustained type (i.e. homogeneous and 'locked in') then the desired volume was added to the coal and the $(NPr_4)(Al_2Et_6)$.n-toluene clathrate was added to make the total liquid clathrate volume 100 ml. The rest of the procedure was as for (a) unless hydrogen gas was to be present during the extraction (see below).

c) In Situ Hydrogenation.

If hydrogen gas was used during the extraction, the procedure would be followed as for (a) or (b) until the reaction flask was removed from the dry box. A constant stream of dried H_2 gas was passed through the mixture during the extraction (see Figure 1 for schematic of the apparatus). After the desired time the flask was removed from the oil bath and allowed to cool under a constant H_2 pressure.

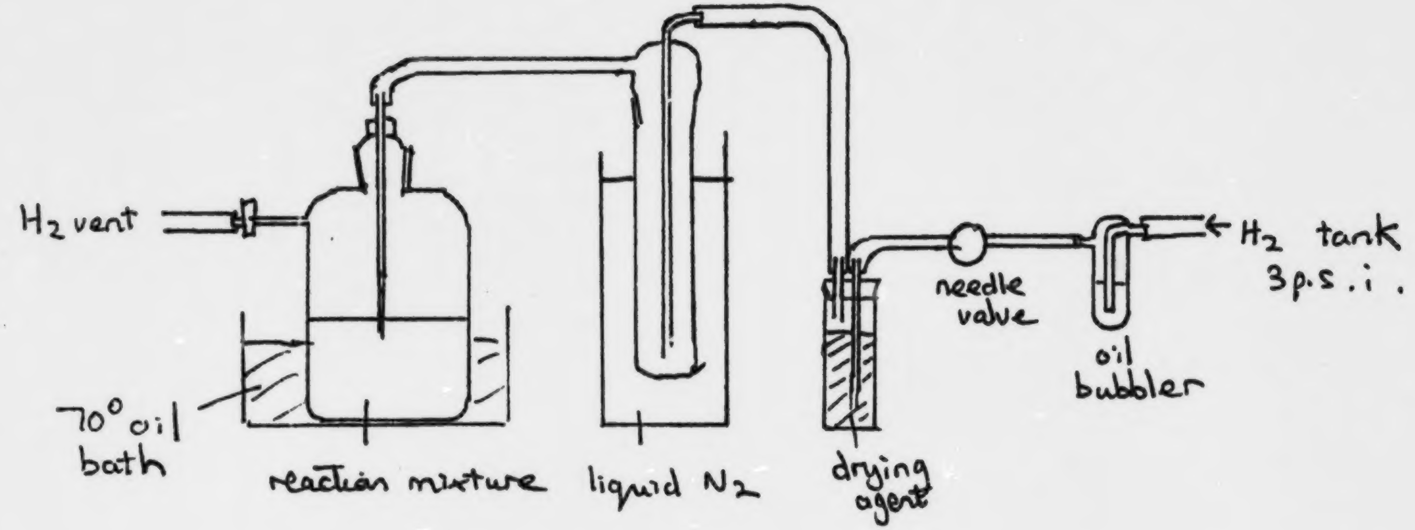

Figure 1. . Schematic of Hydrogenation Apparatus

APPENDIX II.1.5

CONTINUOUS EXTRACTION PROCEDURES

CONTINUOUS EXTRACTION PROCEDURES

Continuous extractions were conducted in a specially designed liquid extractor as depicted schematically in Figure 1. Prior to the introduction of coal and clathrate the apparatus was attached to a vacuum/nitrogen line and the apparatus evacuated and refilled with N_2 several times. The apparatus was kept under a nitrogen atmosphere at all times in the extraction reaction. The coal and 100 ml of clathrate were added to the reaction vessel whilst flushing with nitrogen. Enough toluene (*ca.* 100 ml) was added to bring the total liquid volume to the connecting arm of the flask. A further 100 ml of toluene was placed in the receiving flask. The reaction mixture was stirred gently at 70°C and the toluene in the receiving flask broughtto the boil. During the time of the extraction the apparatus was insulated to improve the recycling rate of the toluene. After the desired amount of extraction time the apparatus was allowed to cool under an excess pressure of N_2.

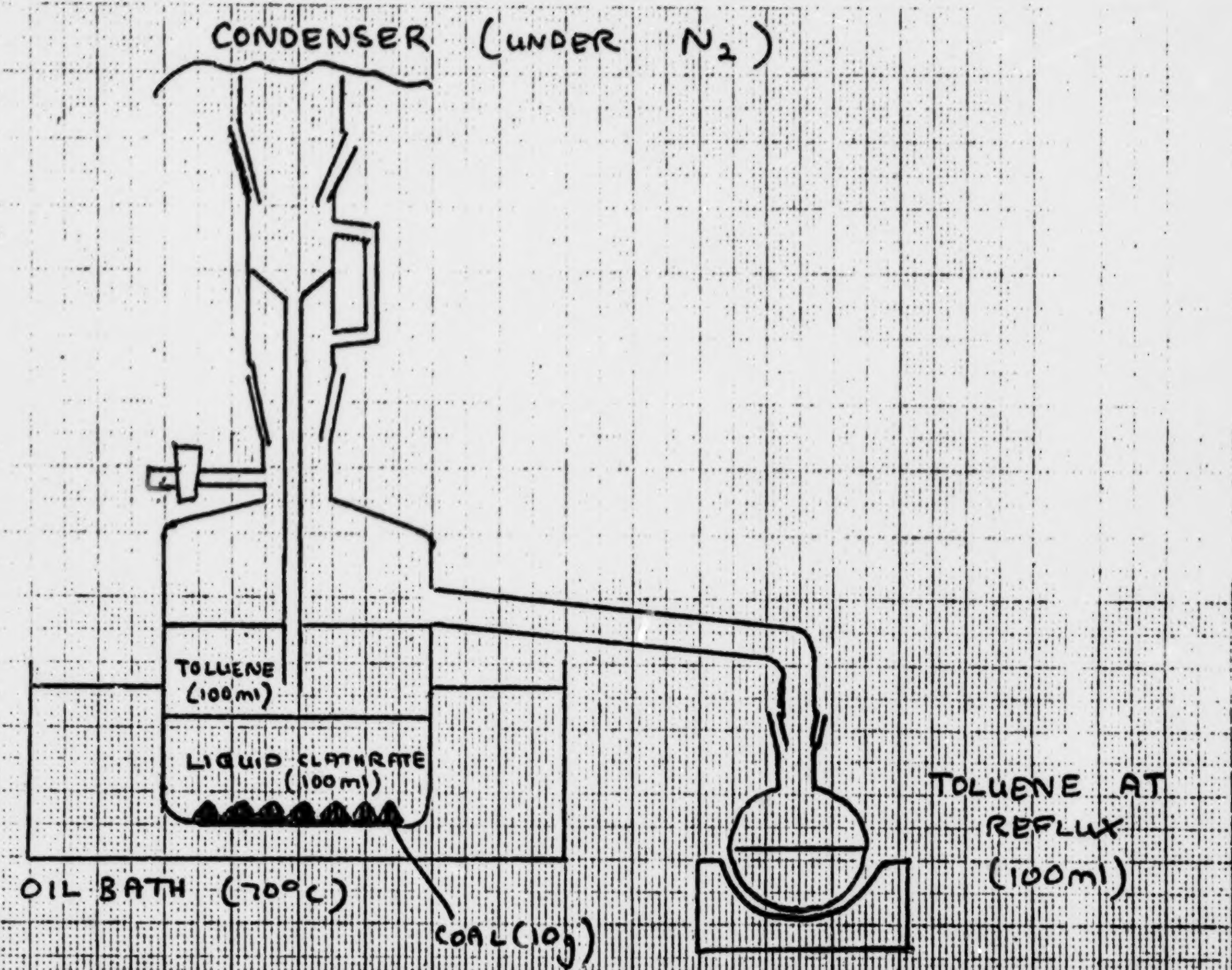

FIGURE 1. SCHEMATIC OF LIQUID-LIQUID EXTRACTOR

APPENDIX II.1.6

DATA TABLES

Table 1a.	Batch extraction trial yields and mass balance.
" 1b.	Results of extraction of various coals with clathrate.
" 2.	Elemental and % ash analyses.
" 3.	% ash analyses.

Table 1a. Batch extraction trial yields and mass balance.

Experiment	Coal	Conditions	Toluene Solubles	Chloroform Solubles		Pyridine Solubles		Total Solubles	Total In-Solubles	Total Recovered	Comments
				B	C	B	C				
2-21#1	K-seam	20 hr, 70°	0.128	0.069	0.130	1.184	0.873	2.384			
2-21#2	K-seam	20 hr, 70°	0.098	0.046	0.123	0.881	1.251	2.399			
2-21#3	K-seam	20 hr, 70°	0.131	0.048	0.106	1.195	0.490	1.970			
2-21#4	K-seam	20 hr, 70°	0.186	0.038	0.146	1.074	0.742	2.186			
2-22	K-seam	20 hr, 70°	0.074	0.046	0.117	1.000	1.116	2.353			CoMo catalyst 1.05g
2-23	K-seam	20 hr, 70°	0.073	0.035	0.098	1.177	0.843	2.226			10% catalyst #6
2-24	K-seam	20 hr, 70°	0.064	0.030	0.104	0.730	0.753	1.681	9.245	10.926	CoMo catalyst 1g
2-25	K-seam	20 hr, 70°	0.055	0.016	0.090	0.254	0.875	1.290	10.229	11.519	10% catalyst #6
2-26	K-seam	20 hr, r.t.						0.971			pyridine only
2-27	K-seam	pyridine reflux						1.101	9.283	10.384	
2-28	K-seam	20 hr continuous extraction	0.271	0.035	0.046	1.090	1.237	2.679	10.036	12.715	
2-29	K-seam	4 hr, 70°, H_2	0.790	0.078	0.787	0.539	0.563	2.757	9.267	12.024	2g catalyst #1, catalyst contamination
2-30	K-seam	4 hr continuous extraction	0.091	0.007	0.041	0.335	0.361	0.835	9.007	9.842	
2-31	K-seam	4 hr, 70°, H_2	0.044	0.034	0.104	0.297	0.511	0.990	9.357	10.347	10% catalyst #6
2-32	K-seam	4 hr, 70°, H_2	0.053	0.028	0.142	0.571	0.370	1.164	9.512	10.676	2g catalyst #3
2-33	K-seam	20 hr, 70°	0.029	0.010	0.037	1.471	0.232	1.779	9.573	11.352	2nd extraction

Experiment	Coal	Conditions	Toluene Solubles	Chloroform Solubles		Pyridine Solubles		Total Solubles	Total In-Solubles	Total Recovered	Comments
				B	C	B	C				
2-34	K-seam	20 hr, 70°	0.089	0.031	0.089	1.299	0.872	2 380	10.873	13.201	
2-35	K-seam	4 hr, 70°, H_2	0.932	0.078	0.863	0.504	0.394	2.811	8.769	11.580	2g catalyst #4. Catalyst contamination.
2-37	K-seam	4 hr, 70°, H_2	0.423	0.106	1.341	0.604	0.300	2.774	9.537	12.311	2g catalyst #2. Catalyst contamination.
2-38	K-seam	20 hr, 70°	0.080	0.077	0.076	1.852	2.332	4.417	9.524	13.941	Pyridine contamination. 50 ml clathrate only.
2-40	K-seam	4 hr, 70°	0.015	0.008	0.035	0.619	0.470	1.147	9.410	10.557	
2-41	K-seam	20 hr, 70°	0.077	0.023	0.121	0.715	1.305	2.241	10.032	12.273	50 ml clathrate only
2-42	K-seam	20 hr, 70°	0.065	0.023	0.145	0.842	1.442	2.517	9.981	12.498	200 ml clathrate
2-43	K-seam	20 hr, 70°	0.052	0.014	0.107	0.660	0.852	1.685	9.404	11.089	50 ml clathrate
2-44	K-seam	20 hr, 70°, H_2	0.163*	0.033	0.253*	1.099	0.663	2.178	9.764	11.942	10% catalyst 5a, * some catalyst contamination
11-2-1	K-seam	20 hr, 70°	0.041	0.019	0.023	0.853	0.696	1.632	11.880	13.512	9.283g pyridine preextracted coal
11-2-2	K-seam	4 hr, 70°, H_2	0.034	0.004	0.069	0.497	0.637	1.241	9.430	10.621	
11-2-3	K-seam	4 hr, 70°	0.549	0.056	0.641	0.387	0.528	2.161	9.197	11.352	2g catalyst #1. Catalyst contamination.
10-1	Devco	20hr, 70°	0.134	0.041	0.176	0.869	1.542	2.762	3.072	5.834	
10-2	Devco	20 hr, 70°	0.098	0.067	0.151	1.151	2.153	3.620	9.256	12.876	
10-3	Devco	4 hr, 70°, H_2	0.904	0.148	1.050	0.491	2.941	5.423	7.840	13.263	2g catalyst #1. Catalyst contamination.
10-4	Devco	4 hr, 70°, H_2	0.118	0.011	0.077	0.367	0.928	1.501	8.581	10.082	0.25 g catalyst #1. Catalyst contamination.
10-5	Devco	20 hr, 70°	0.131	0.071	0.251	1.234	--	--	--	--	Pyridine fraction lost.
10-6	Devco	4 hr, 70°, H_2	0.855	0.064	1.024	0.644	0.624	3.211	8.191	11.402	2 ml catalyst #16. Catalyst contamination.

Exper-iment	Coal	Conditions	Toluene Solubles	Chloroform Solubles		Pyridine Solubles		Total Solubles	Total In-solubles	Total Recov-ered	Comments
				B	C	B	C				
10-7	Devco	20 hr, 70°	0.120	0.027	0.149	0.884	2.082	3.262	8.126	11.388	
10-8	Devco	20 hr, 70°	0.068	0.033	0.067	1.244	1.530	2.909	9.327	12.269	2nd extraction - uncorrected for residues used
10-9	Devco	20 hr, 70°	0.068	0.021	0.176	0.631	1.773	2.648	8.383	11.031	200 ml clathrate
10-10	Devco	20 hr, 70°	0.117	0.064	0.093	1.209	0.945	2.364	6.248	8.612	50 ml clathrate
10-11	Devco	4 hr, 70°	0.048	0.023	0.077	0.798	0.831	1.777	7.734	9.511	
10-12	Devco	20 hr, 70°, H_2	0.191*	0.013	0.210*	0.857	1.913	3.184	8.768	11.952	10% catalyst 5a, * some catalyst contamination
11-10-1	Devco	4 hr, 70°, H_2	0.026	0.009	0.049	1.504	0.626	2.214	8.337	10.551	
11-10-3	Devco	Toluene, pyridine soxhlet, 20 hr	0.026			0.861		0.887	9.805	10.692	
11-10-4	Devco	20 hr, 70°, H_2	0.113	0.043	0.142	1.045	2.231	3.574	8.461	12.035	
12-1	K-seam/ Devco	20 hr, 70°	0.086	0.036	0.138	0.972	2.232	3.464	8.876	12.340	5g K-seam, 5g Devco
12-2	K-seam/ Devco	20 hr, 70°	0.108	0.032	0.196	0.555	2.260	3.151	9.194	12.345	5g K-seam, 5g Devco
12-3	K-seam/ Devco	20 hr, 70°	0.100	0.007	0.096	0.879	1.792	2.874	9.491	12.365	8g K-seam, 2g Devco
12-4	K-seam/ Devco	20 hr, 70°	0.097	0.051	0.144	0.852	1.693	2.837	9.629	12.466	8g K-seam, 2g Devco
12-5	K-seam/ Devco	20 hr, 70°	0.085	0.028	0.135	0.871	1.372	2.491	10.166	12.657	9g K-seam, 1g Devco
12-6	K-seam/ Devco	20 hr, 70°	0.135	0.038	0.170	0.700	--*	--	--	--	9g K-seam, 1g Devco *sample lost

Experiment	Coal	Conditions	Toluene Solubles	Chloroform Solubles		Pyridine Solubles		Total Solubles	Total Insolubles	Total Recovered	Comments
				B	C	B	C				
9-1	Illinois #6	20 hr, 70°	0.033	0.031	0.076	1.467	0.418	1.992			
9-2	Illinois #6	20 hr, 70°	0.031	0.021	0.019	1.285	0.356	1.712	8.872	10.589	some clathrate
11-9-1	Illinois #6	20 hr, soxhlet	0.030			1.019		1.049	9.827	10.876	toluene then pyridine soxhlets
13-1	Quinsam	20 hr, 70°	0.035	0.016	0.013	0.479	0.444	0.987	8.661	9.648	
13-2	Quinsam	20 hr, 70°	0.021	0.012	0.039	1.167	0.413	1.652	8.811	10.463	
13-3	Quinsam	20 hr, 70°	0.053	0.039	0.052	0.595	0.435	1.174	8.800	9.974	
11-13-1	Quinsam	20 hr, soxhlet	0.038				0.462	0.500	10.391	10.891	toluene then pyridine soxhlets
14-1	Mary Lee	20 hr, 70°	0.083	0.036	0.184	1.429	1.504	3.236	9.061	12.297	
14-2	Mary Lee	20 hr, 70°	0.119	0.029	0.182	0.920*	1.230	2.480	8.866	11.346	*sample lost during vacuum distillation
11-14-1	Mary Lee	20 hr, soxhlet	0.017				1.670	1.687	9.013	10.700	

Table 1b. **Results of Extraction of Various Coals with Clathrate**

Experiment No.	Coal	Clathrate	Extraction Conditions	Wt. of Coal (g)	Wt. of tol. sol.(g)	Wt. of pyr. sol.(g)	Wt. CH_2Cl_2 sol.(g)	% Conversion Toluene sol.	% Conversion Pyridine sol.	% Conversion CH_2Cl_2 sol.
0-10	K seam	--	17 hr toluene soxhlet followed by 17 hr pyridine reflux	10.0 g	—	1.114		--	11.1%	
0-11	K seam	--	17 hr toluene soxhlet followed by pyridine reflux	10.0 g	0.049	1.382		0.49%	13.8	
0-12										
0-13	K seam	—	17 hr toluene soxhlet	10.0 g	0.085			0.85		
0-14										
0-15	Hat Creek	--	17 hr toluene soxhlet	10.0 g	0.039			0.39		
0-16	Hat Creek	--	17 hr pyridine soxhlet	10.0 g		0.287			2.87	
0-17	Forestburg	--	17 hr toluene soxhlet	9.5 g	0.017			0.18		
0-18	Forestburg	--	17 hr pyridine soxhlet	10.1 g		0.354			3.50	
0-19										
0-20	Merritt	--	17 hr toluene soxhlet	10.2 g	0.059			0.57		
0-21	Merritt	--	17 hr pyridine soxhlet	10.2 g		0.998			9.78	
0-22	Telkwa	--	17 hr toluene soxhlet	10.1 g	0.058			0.57		
0-23	Telkwa	--	17 hr pyridine soxhlet	10.0 g		0.721			7.21	
0-24	Merritt	--	17 hr CH_2Cl_2 soxhlet	10.2 g			0.083			0.81
2-9	K seam	$[Pr_4N][(Et_3Al)_2I]$: Toluene	70°C, 50 ml extractions, for two weeks	10.0	0.776	--		7.76	—	
2-10	K seam	"	coal redried, same conditions one day	10.0	0.731*	1.321		7.31*	13.2	
2-11	K seam	"	70°C, hydrogenation	10.0	0.11†	—		1.1†	—	
2-12	K seam	"	70°C, hydrogenation	10.0	0.854	0.982		8.54	9.82	

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Table 1b. continued

Experiment No.	Coal	Clathrate	Extraction Conditions	Wt. of Coal (g)	Wt. of tol. sol. (g)	Wt. of pyr. sol. (g)	Wt. CH_2Cl_2 sol. (g)	% Conversion		
								Toluene sol.	Pyridine sol.	CH_2Cl_2 sol.
3-1	K seam	$[Me_4N][(Et_3Al)_2I]$: Toluene	10 g coal, 55 ml clathrate, 55 ml toluene, 70°C for 10 days	10.0	1.388	0.348		13.9	3.48	
4-1	Forestburg	$[Pr_4N][(Et_3Al)_2I]$: Toluene	1 g coal, 10 ml clathrate, 10 ml toluene	1.0	--					
4-2	Forestburg	"	hydrogenation, 100 ml clathrate and toluene	10.0	--					
5-1	Hat Creek	"	1 g coal, 10 ml clathrate and 10 ml toluene	1.0	--					
3-2	Hat Creek	"	100 ml clathrate and toluene, acid washed H.C. coal	10.0	--					
6-1	Telkwa	"	1 g coal, 10 ml clathrate and 10 ml toluene	1.0	.023			2.3		
6-2	Telkwa	"	100 ml toluene and clathrate	10.0	0.287	0.394	--	2.87	3.94	--
7-1	Merritt	"	10 ml clathrate and 10 ml toluene	1.0	.066			6.6		
7-2	Merritt	"	100 ml toluene and clathrate	10.0	0.343	0.257	.136	3.43	2.57	1.36
6-3	Telkwa	"	" " " "	10.0						
7-3	Merritt	"	" " " "	10.0						

* Inorganic contamination in this figure

† Preliminary only

** Clathrate not correct

Table 1b. continued

Experiment No.	Coal	Clathrate	Extraction Conditions	Wt. of Coal (g)	Wt. of tol. sol. (g)	Wt. of pyr. sol. (g)	Wt. $CHCl_3$ sol. (g)	% Conversion		
								Toluene sol.	Pyridine sol.	$CHCl_3$ sol.
2-13	K seam	—	150 ml toluene, ml Et_3Al	10.0	0.309	—		3.09	—	
2-14	K seam	$[Pr_4N][(Et_3Al)_2I]$: Toluene	70°C, 50 ml extractions		0.745	1.372		7.45	13.72	
2-16	K seam	"		10.0	0.349	0.988		3.49**	9.88	
2-17	K seam(Ar)	"		10.0	0.686	0.861		6.86	8.61	
2-18	K seam	"	70°C, 50 ml extractions	10.0	0.728	1.363		7.28	13.63	
2-19	K seam(Ar)	"	" " " "	10.0	0.772	1.470		7.72	14.70	
2-20	K seam (acid washed)	"	" " " "	10.0	0.501	0.676	0.853	5.01	6.76	8.53

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Table 2. % Ash analyses

Sample type	Coal	Experiment No.	Experiment Description	Weight of Material Ignited (g)	% Ash
coal	K-seam	--	--	1.2978	3.56
coal	K-seam	--	--	2.2735	3.35
coal	Merritt	--	--	1.3414	21.2
coal	Devco 1	--	--	0.8743	1.23
coal	Devco 1	--	--	1.1999	1.24
coal	Devco 1	--	--	1.2952	1.20
coal	Devco 2	--	--	0.7664	5.39
coal	Devco 2	--	--	0.8978	5.60
coal	Mary Lee	--	--	0.6084	13.67
coal	Mary Lee	--	--	0.5256	13.64
coal	Illinois #6	--	--	0.9650	10.72
coal	Illinois #6	--	--	0.9081	10.68
coal residue	K-seam	2-26	pyridine soxhlet	0.3510	3.20
coal residue	K-seam	2-22	clathrate, 1.05 g CoMo, 20 hours, 70°C	--	14.58
coal residue	K-seam	2-24#3	clathrate, 1.0 g CoMo, 20 hours, 70°C	0.8458	9.56
coal residue	K-seam	2-25	clathrate, 10% $[Fe(C_5H_5)(arene)]^+$, H_2 20 hours, 70°C	0.3443	12.08
coal residue	K-seam	2-28	clathrate, continuous extraction, 20 hours, 70°C	0.5843	11.12

Table 2. continued.

Sample type	Coal	Experiment No.	Experiment Description	Weight of Material Ignited (g)	% Ash
coal residue	K-seam	2-29	clathrate, 2.0 g $Mn(C_5H_5)(CO)_3$, H_2, 4 hours, 70°C	0.6303	3.40
coal residue	K-seam	2-34	clathrate, 20 hours, 70°C	0.3905	6.50
coal residue	K-seam	2-41	50 ml clathrate, 20 hours, 70°C	1.1177	4.36
coal residue	K-seam	2-42	200 ml clathrate, 20 hours, 70°C	1.0182	5.43
coal residue	Illinois #6	9-1	clathrate, 20 hours, 70°C	0.2573	9.17
coal residue	Illinois #6	9-2	clathrate, 20 hours, 70°C	0.7196	8.64
coal residue	Devco	10-1	clathrate, 20 hours, 70°C	0.3014	6.37
coal residue	Devco	10-2	clathrate, 20 hours, 70°C	0.2721	10.14
coal residue	Devco	10-3	clathrate, 2.0 g $Mn(C_5H_5)(CO)_3$, H_2, 4 hours, 70°C	0.3827	4.89
coal residue	Devco	10-4	clathrate, 0.25 g $Mn(C_5H_5)(CO)_3$, H_2, 4 hours, 70°C	--	1.92
coal residue	Devco	10-5	clathrate, 20 hours, 70°C	0.3280	8.57
coal residue	Devco	10-6	clathrate, 2 ml $Mn(MeC_5H_4)(CO)_3$, H_2, 4 hours, 70°C	0.6610	3.12
coal residue	Devco	10-7	clathrate, 20 hours, 70°C	0.1622	5.36
coal residue	pyridine extracted K-seam	11-2-1	clathrate, 20 hours, 70°C	0.3250	14.28
coal residue	K-seam	11-2-2	clathrate, H_2, 4 hours, 70°C	0.1252	4.15
coal residue	Devco	11-10-1	clathrate, H_2, 4 hours, 70°C	0.2116	2.79

Table 2. continued.

Sample type	Coal	Experiment No.	Experiment Description	Weight of Material Ignited (g)	% Ash
coal residue	Mary Lee	14-1	clathrate, 20 hours, 70°C	1.0210	19.18
clathrate residue	K-seam	2-22	clathrate, 1.05 g CoMo, 20 hours, 70°C	0.1473	12.29
clathrate residue	K-seam	2-25	clathrate, 10% $[Fe(C_5H_5)arene]^+$, H_2, 20 hours, 70°C	0.1182	9.22
clathrate residue	K-seam	2-28	clathrate, continuous extraction, 20 hours, 70°C	0.4118	11.17
clathrate residue	K-seam	2-29	clathrate, 2.0 g $Mn(C_5H_5)(CO)_3$, H_2, 4 hours, 70°C	0.2674	4.04
clathrate residue	K-seam	2-34	clathrate, 20 hours, 70°C	0.2841	6.69
clathrate residue	K-seam	2-41	50 ml clathrate, 20 hours, 70°C	1.2212	4.85
clathrate residue	K-seam	2-42	200 ml clathrate, 20 hours, 70°C	1.4192	6.67
clathrate residue	Illinois #6	9-1	clathrate, 20 hours, 70°C	0.1115	12.91
clathrate residue	Illinois #6	9-2	clathrate, 20 hours, 70°C	0.2573	11.54
clathrate residue	Devco	10-1	clathrate, 20 hours, 70°C	--	6.20
clathrate residue	Devco	10-2	clathrate, 20 hours, 70°c	0.2014	10.77
clathrate residue	Devco	10-3	clathrate, 2.0 g $Mn(C_5H_5)(CO)_3$, H_2, 4 hours, 70°C	0.2833	8.22
clathrate residue	Devco	10-4	clathrate, 0.25 g $Mn(C_5H_5)(CO)_3$, H_2, 4 hours, 70°C	--	1.78
clathrate residue	Devco	10-6	clathrate, 2 ml $Mn(MeC_5H_4)(CO)_3$, H_2, 4 hours, 70°C	0.4232	2.98
clathrate residue	Devco	10-7	clathrate, 20 hours, 70°C	0.7358	5.65

Table 2. continued.

Sample type	Coal	Experiment No.	Experiment Description	Weight of Material Ignited (g)	% Ash
clathrate residue	pyridine extracted K-seam	11-2-1	clathrate, 20 hours, 70°C	0.2099	9.86
clathrate residue	K-seam	11-2-2	clathrate, H_2, 4 hours, 70°C	0.1041	4.90
clathrate residue	Devco	11-10-1	clathrate, H_2, 4 hours, 70°C	0.4483	2.30
clathrate residue	Mary Lee	14-1	clathrate, 20 hours, 70°C	0.5972	13.26

Table 3. Elemental and % ash analyses

No.	Type	Sample Coal	Experiment Description	Results (%) C	H	S	Ash
10-3B	coal residue	Devco	4 hours, 70°C	77.73	5.38	0.59	4.89
10-3C	clathrate residue	Devco	4 hours, 70°C	70.21	4.98	0.50	8.22
10-4B	coal residue	Devco	4 hours, 70°C, H_2	82.90	5.41	0.57	1.92
10-4C	clathrate residue	Devco	4 hours, 70°C, H_2	82.76	5.37	0.53	1.78
Devco	coal	Devco		84.49	5.39	0.70	1.23
2-29B	coal residue	K-seam	4 hours, 70°C, H_2	80.87	4.91	0.56	3.40
2-28C	clathrate residue	K-seam	20 hours, 70°C, continuous	65.95	4.59	0.36	11.17
2-29C	clathrate residue	K-seam	4 hours, 70°C, H_2	77.75	4.62	0.46	4.04
2-28B	coal residue	K-seam	20 hours, 70°C, continuous	68.37	4.66	0.41	11.17
11-2-1C	clathrate residue	K-seam	20 hours, 70°C	66.63	4.98	0.28	9.86
11-2-1B	coal residue	K-seam	20 hours, 70°C	62.26	4.76	0.22	14.28
9-1-B	coal residue	Illinois #6	20 hours, 70°C	67.92	4.58	2.85	9.17
11-2-2C	clathrate residue	K-seam	4 hours, 70°C, H_2	66.85	4.82	0.43	4.90
11-2-2B	coal residue	K-seam	4 hours, 70°C, H_2	61.36	4.75	0.31	4.15
RC7	coal	Illinois #6		66.73	4.49	3.04	
9-1-C	clathrate residue	Illinois #6	20 hours, 70°C	63.76	4.58	1.86	12.91
2-22C	clathrate residue	K-seam	20 hours, 70°C	64.08	4.47	0.43	12.29
2-22B	coal residue	K-seam	20 hours, 70°C	66.74	4.37	0.44	
RC6	coal	Illinois #6		67.13	4.51	3.11	
2-9A	toluene solubles	K-seam	2 week sequential, 70°C	75.76	7.35		
2-14BA	toluene extract of coal residue	K-seam	2 week sequential, 70°C	75.21	5.46		
2-14CA	toluene extract of clathrate residue	K-seam	2 week sequential, 70°C	77.96	5.80		

APPENDIX II.1.7

REMOVAL OF SOLVENTS BY VACUUM DISTILLATION

REMOVAL OF SOLVENTS BY VACUUM DISTILLATION

The Apparatus:

The apparatus consisted of a vacuum pump, solvent trap, vacuum/nitrogen manifold, nitrogen supply and distillation glassware.

The vacuum pump was a Precision Model D-25. Approximately 50cm of 5/8" OD vacuum tubing connected the pump to the solvent trap. The sidearm of the trap was connected to the vacuum/nitrogen manifold (Figure 1). The 3-way valve of the manifold could be: closed, open to nitrogen or open to vacuum. The vacuum manifold was connected to the nitrogen manifold with 3/8" OD vacuum tubing. A needle valve controlled the flow of nitrogen which could be directed to flasks on the vacuum line or diverted from the system. The nitrogen manifold was connected via 1/4" OD tygon tubing to 2 x 250 ml dreschel bottles, the second of which was half filled with glycerin to indicate nitrogen flow. The first dreschel bottle (empty) provided a trap to prevent glycerin from entering the manifold. Each outlet on the vacuum manifold was connected to a 3-way valve via 1/4" OD vacuum tubing. A vacuum receiver adapter was connected to one valve via vacuum tubing. The tubing from another valve was connected to 1 metre of 1/4" OD rubber tubing. This served as the nitrogen bleed into the still pot.

The glassware included: a still head with B24 joints and B10 thermometer joint, a Fisher scientific -10 to 360°C thermometer with B10 ground glass joint; B24 Liebeg condenser; vacuum receiver adapter with B24 joints and 500 ml round bottom receiver flask with B24 neck. The preparation of the sample flask is discussed below. Other equipment: a 250 Glas-col heating mantle, 1.4KVA voltage regulator, 2 o-rings, 2 clamps and one 2ℓ metal bowl or pan with high sides.

Preparation of the Sample Flask:

A modified Pasteur pipette was inserted into the sidearm of the distillation flask through a thermometer adaptor to deliver a stream of N_2 into the sample during the course of the distillation. A bunsen burner and long forceps were used to pull out the tip of a Pasteur pipette to a fine point. Several pipettes were prepared at one time as 5 per experiment were required.

A clean, dry, labelled 250 ml 2 neck (B19, B24) round bottom flask was pre-weighed for the distillation flask. The cap of a B19 thermometer adapter was unscrewed and the rubber washer removed. The washer was slid over the tip of the Pasteur pipette and pulled along its length until about 7 cm from the wide end. The thermometer adapter was inserted into the B19 neck (sidearm) of the flask. The pipette was inserted into the adapter and the rubber washer adjusted so that the tip of the pipette rested on the bottom of the flask. The lid was screwed on to the adapter and tightened.

Distillation Procedure:

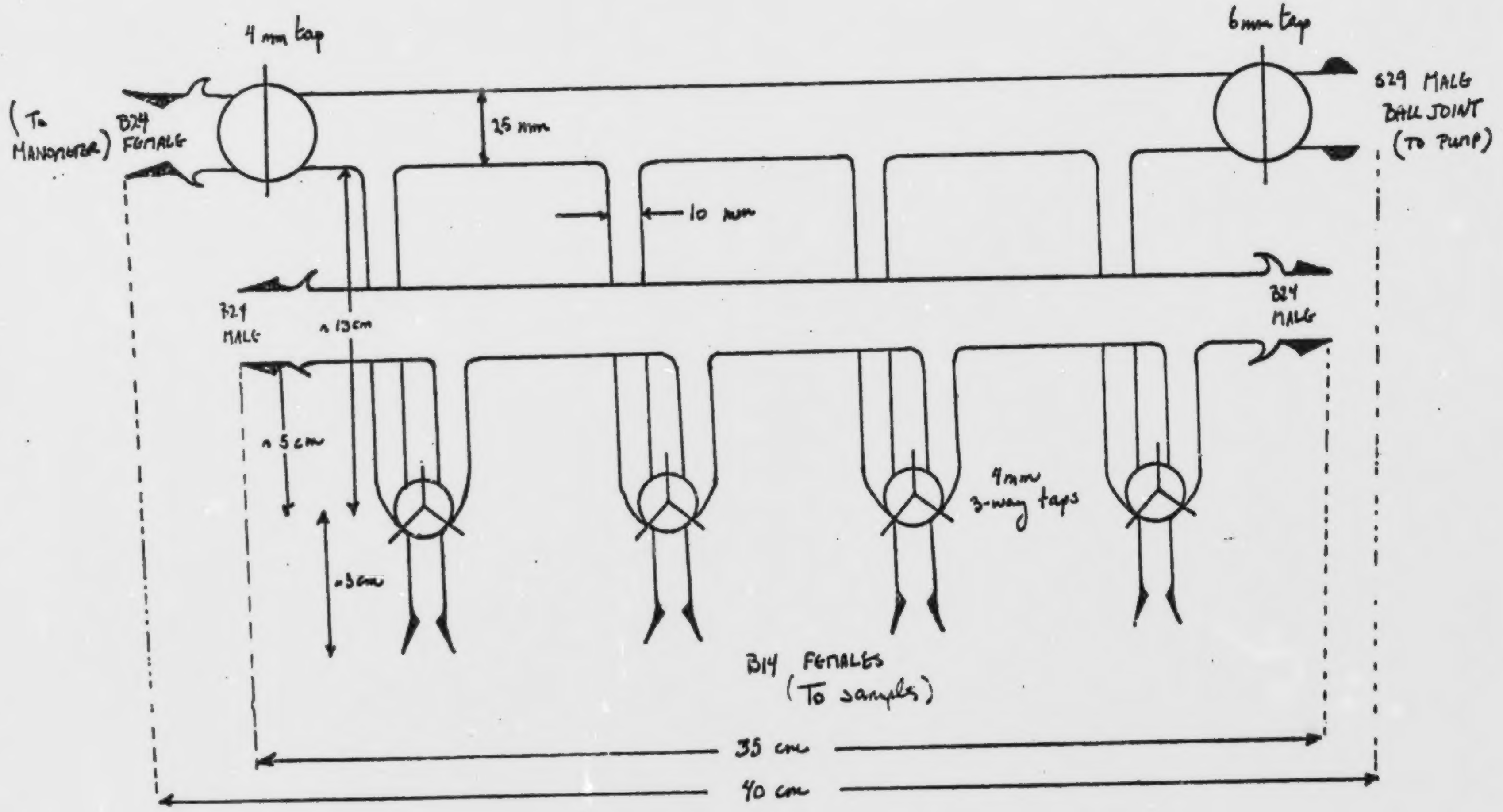
The distillation glassware was assembled as shown in Figure 2 and attached to the vacuum manifold. When the vacuum line was not in use all valves on the manifold were closed. When setting up the distillation glassware the first step was to clamp the receiver flask to the metal support rods on the bench. It was clamped so that the bottom of the flask just touched the bottom of the metal bowl set under it. The bowl was filled with sufficient crushed dry ice to cover the flask. Acetone was poured into the bowl to form an acetone/dry ice slurry. The colder the receiver flask the less time the distillation took. Once the receiver flask began to cool, the flask containing sample was clamped to the metal support beams. (Because of the angles in the glassware the sample flask should be about 15 cm higher than the receiver flask.) The vacuum receiver adapter sat in the receiver flask and a cold water condenser was inserted into the adapter. The nitrogen bleed was opened and the tubing slipped over the end of the Pasteur pipette. To control the rate of N_2 delivery a tubing clamp was tightened on the nitrogen line until bubbling in the flask was barely discernible.

With the vent on the vacuum manifold closed the vacuum pump was started. A dewar flask half filled with liquid nitrogen was placed over the trap and supported by an O-ring clamped to the metal rods. The dewar flask was then topped up with nitrogen. The valve to the receiver adapter was opened slowly to vacuum. When the system was evacuated the sample began to bubble vigorously. The vacuum and flow of nitrogen were adjusted so that the sample bubbled but did not splash and the flask began to cool. If the vacuum was too great the sample "bumped" over to the receiver flask. When vacuum and nitrogen bleed were adjusted, the heating mantle was set under the flask and held in place by an O-ring clamped to the support rods. The voltage regulator on the heating mantle was turned on, set at slightly less than 30.

The distillation was checked periodically to ensure the correct vacuum/nitrogen ratio for maximum efficiency. This was determined by a slow, even bubbling of the sample being distilled.

Vacuum distillation of the toluene (A) fraction took approximately 30 minutes, the chloroform fractions (B and C) 20 minutes and the cold pyridine fractions 1 hour 30 minutes to 2 hours.

When the solvent had been distilled the heating mantle was removed and the valve to the vacuum line closed. The flow of nitrogen was increased at the needle valve and the tubing clamp slowly opened until the system filled with nitrogen to atmospheric pressure. The flow of nitrogen was decreased and the valve closed. The rubber tubing was removed from the pipette and the flask removed from the distillation apparatus. The flask containing sample was weighed when it came to room temperature.



VACUUM/N$_2$ MANIFOLD.

Figure 1.

Vacuum/Nitrogen Manifold

Scale: 1cm = 2.0cm

28/4/81 I.C

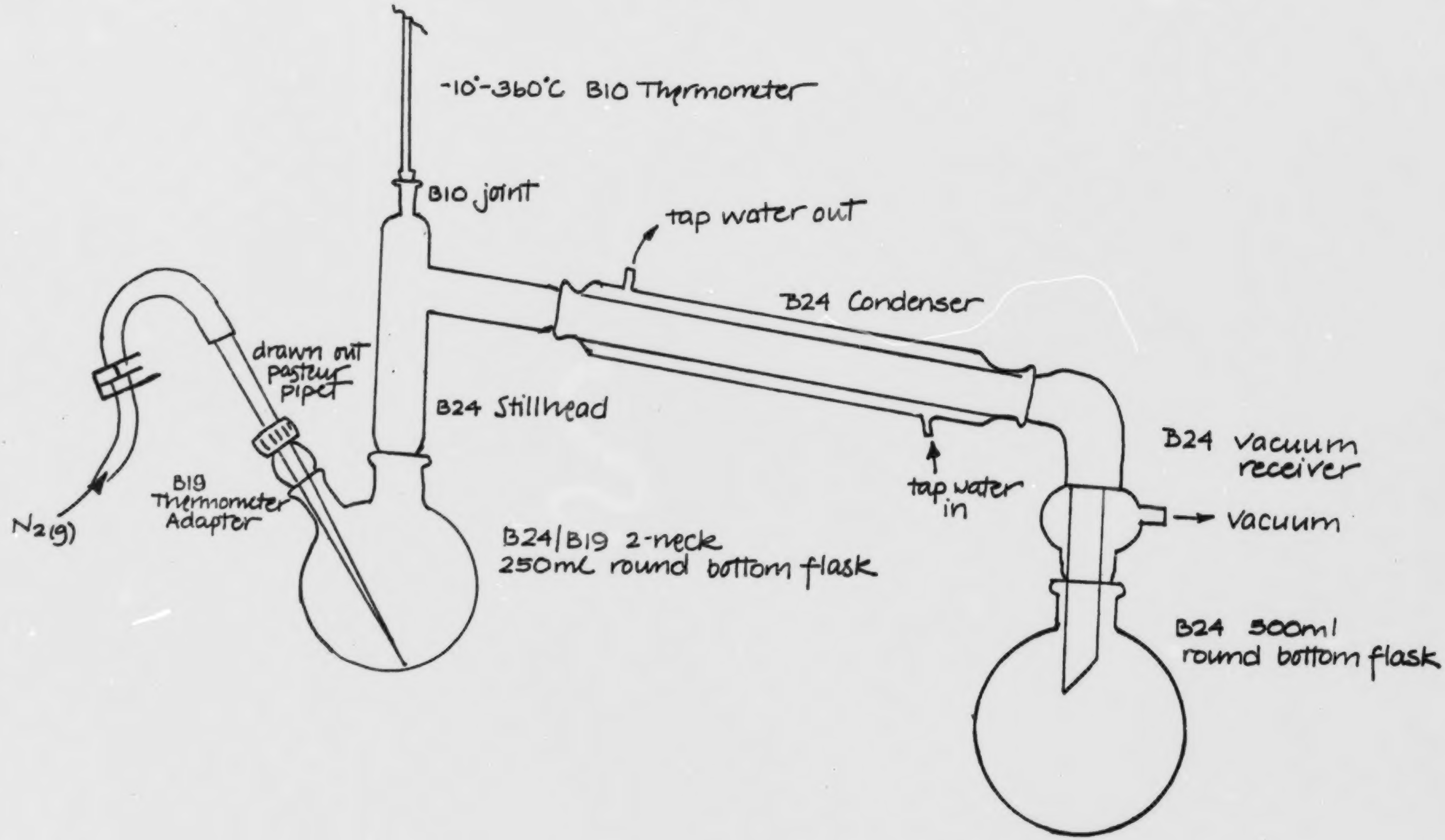


Figure 2.

Distillation Glassware

APPENDIX II.1.8

RESULTS OF SEQUENTIAL EXTRACTIONS

a) Toluene Solubles versus time

b) NMR data: Aromatic/Aliphatic ratios versus time

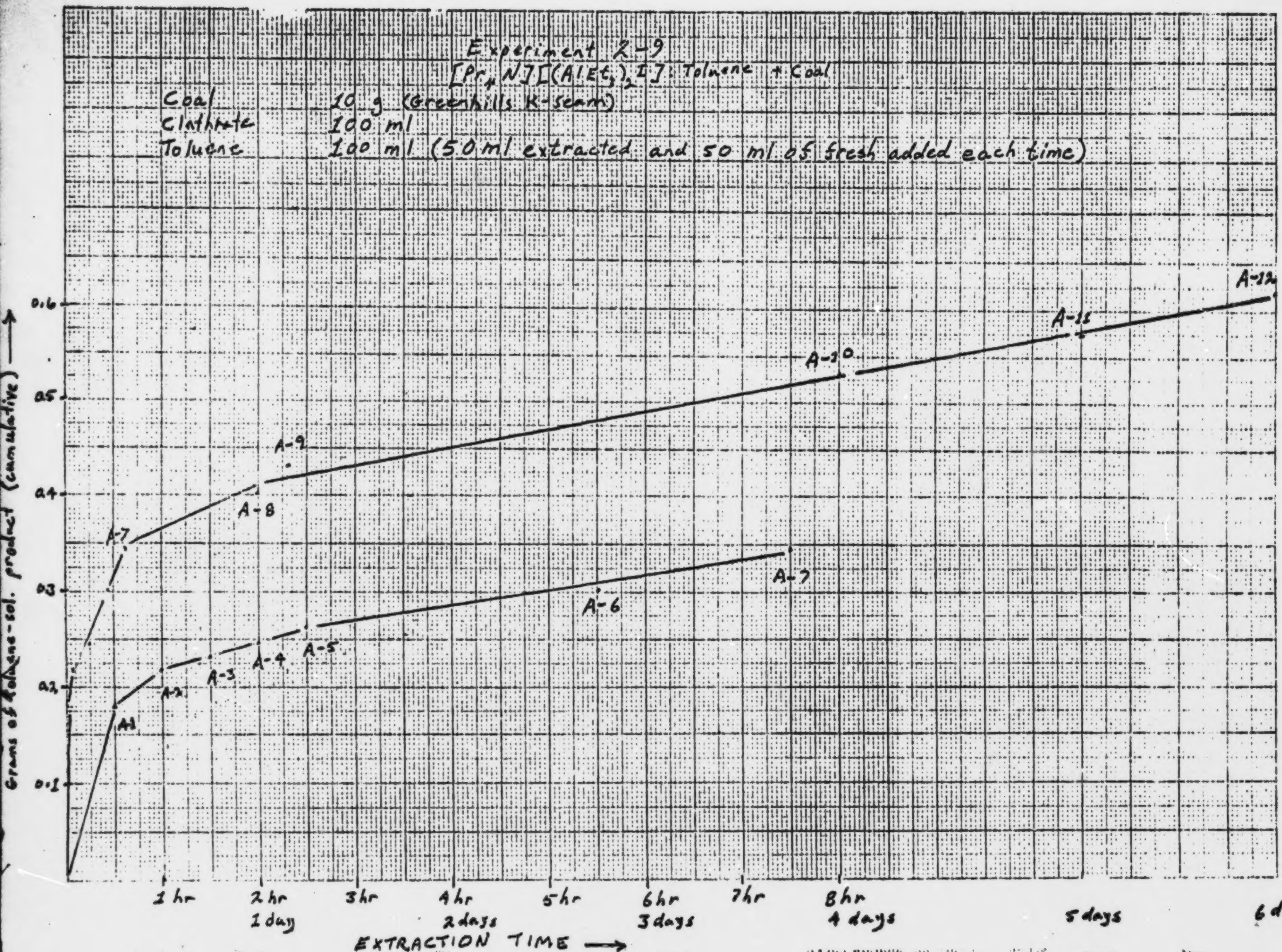
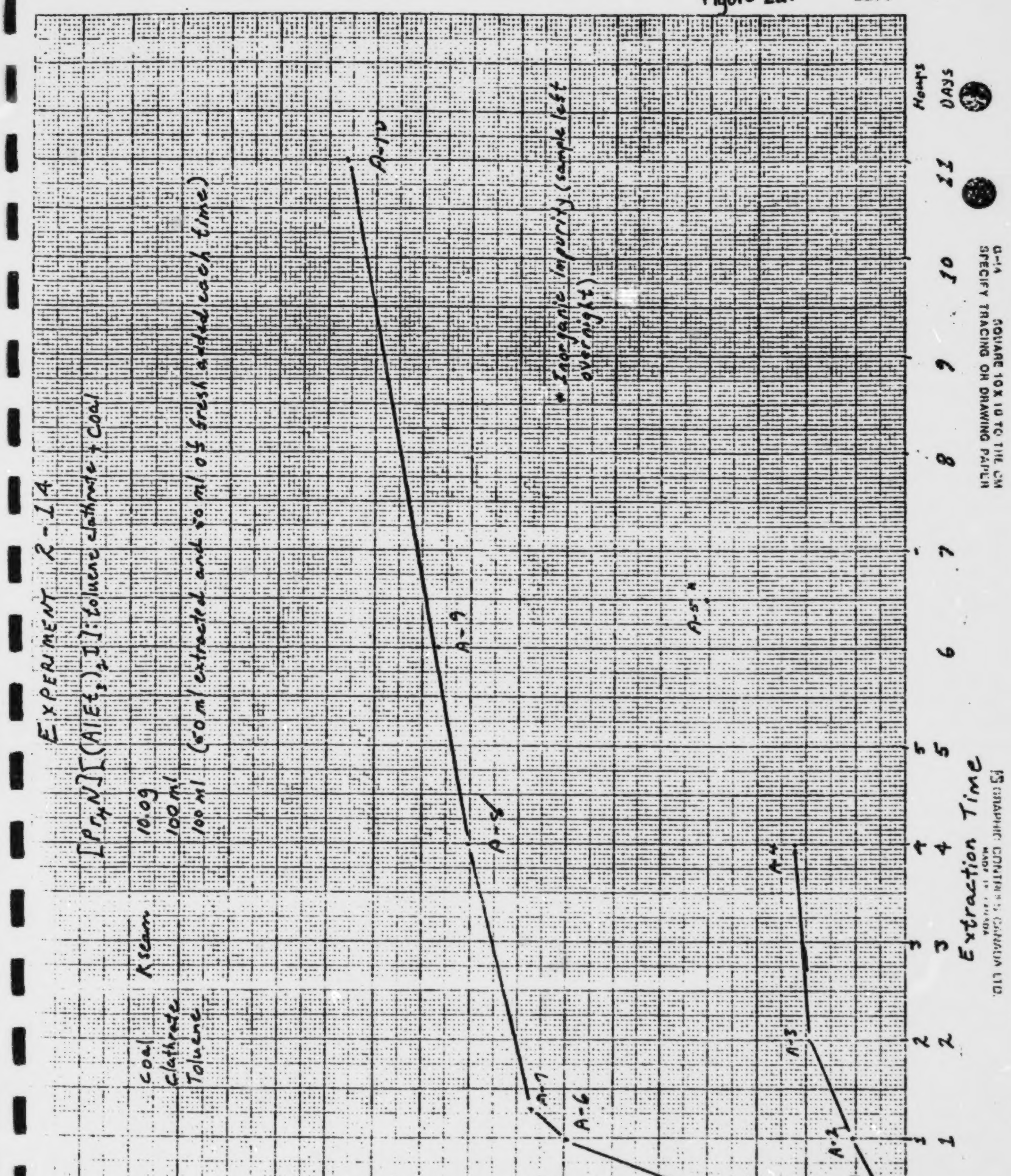
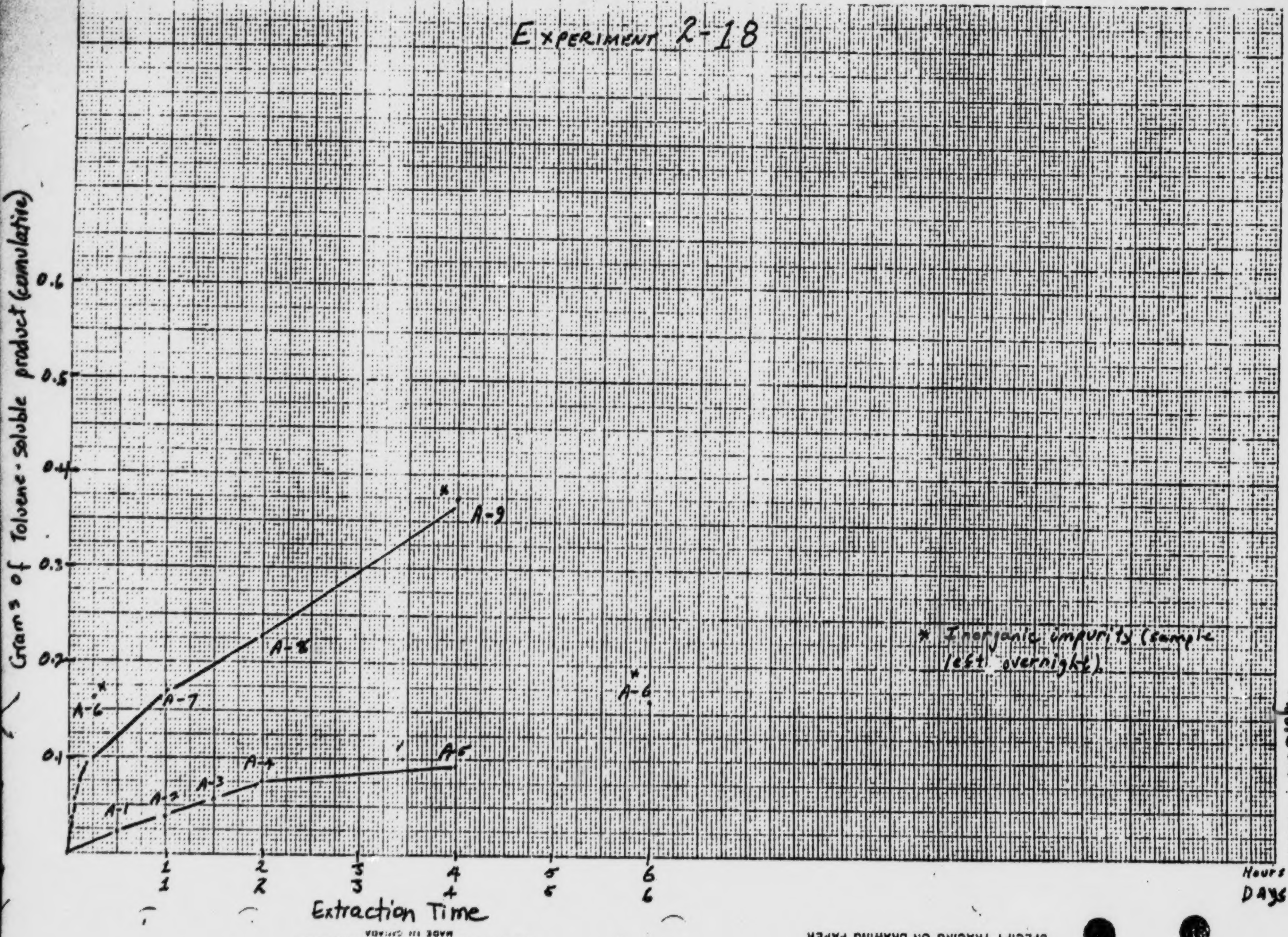


FIGURE 1a. 116.

Figure 2a. 117.



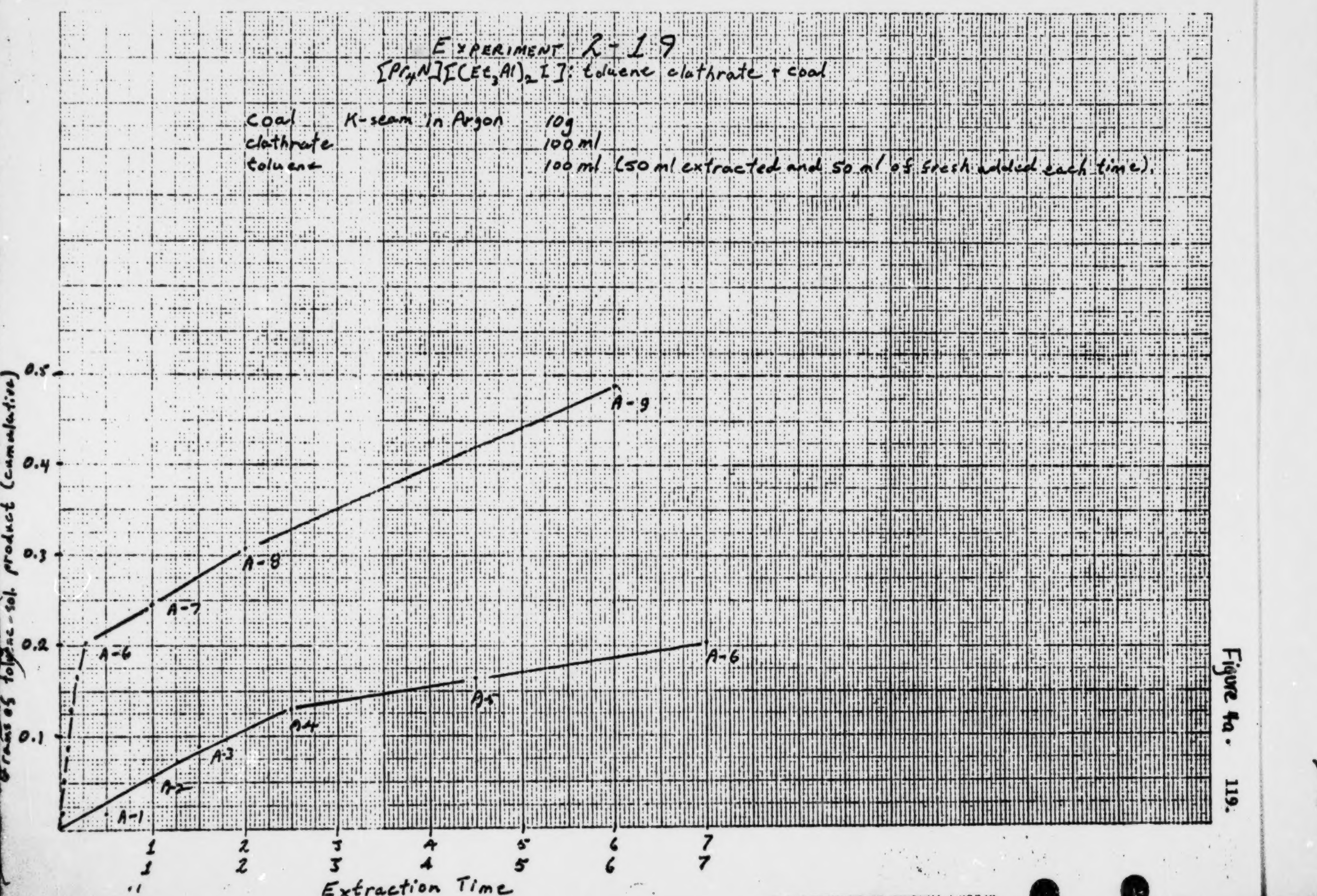


* Inorganic impurity (sample left overnight).

Figure 3a.

G-14 SQUARE 10 X 10 TO THE CM
SPECIFY TRACING OR DRAWING PAPER
GRAPHIC CONTROLS CANADA LTD.
MADE IN CANADA

Figure 4a.



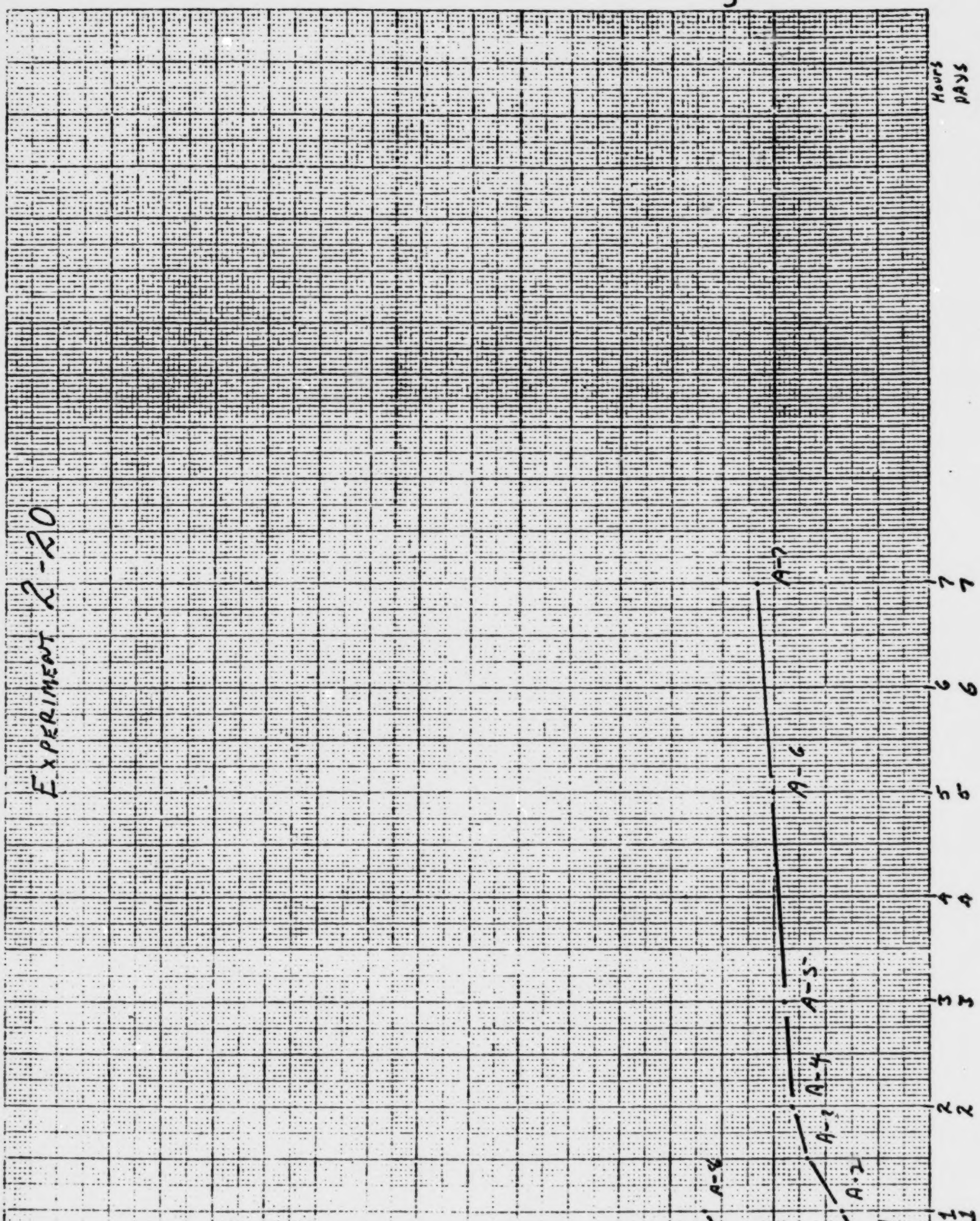
EXPERIMENT 2-19

$[Pr_4N][(Et_3Al)_2I]$: toluene clathrate + coal

coal	K-seam in Argon	10g
clathrate		100 ml
toluene		100 ml (50 ml extracted and 50 ml of fresh added each time).

SQUARE 10X10 TO THE CM
SPECIFY TRACING OR DRAWING PAPER
G-14
GRAPHIC CONTROLS
MADE IN CANADA

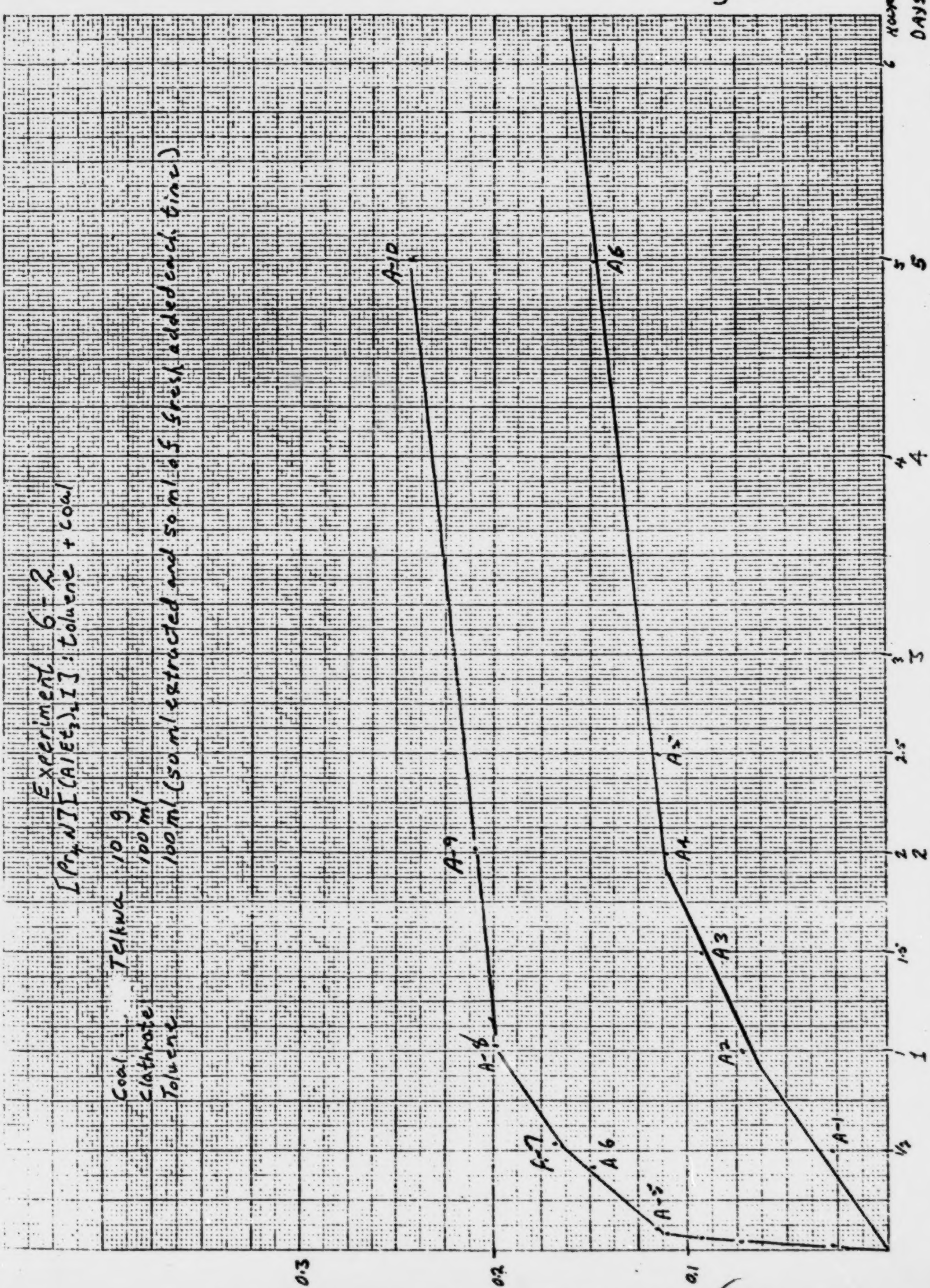
Figure 5a.



0-14 SQUARE 10X10 TO THE CM
SPECIFY TRACING OR DRAWING PAPER

GRAPHIC CONTROLS CANADA LTD.
MADE IN CANADA

Figure 6a.



G-14 SQUARE 10 X 10 TO THE CM
SPECIFY TRACING OR DRAWING PAPER
GRAPHIC CONTROLS CANADA LTD
MADE IN CANADA

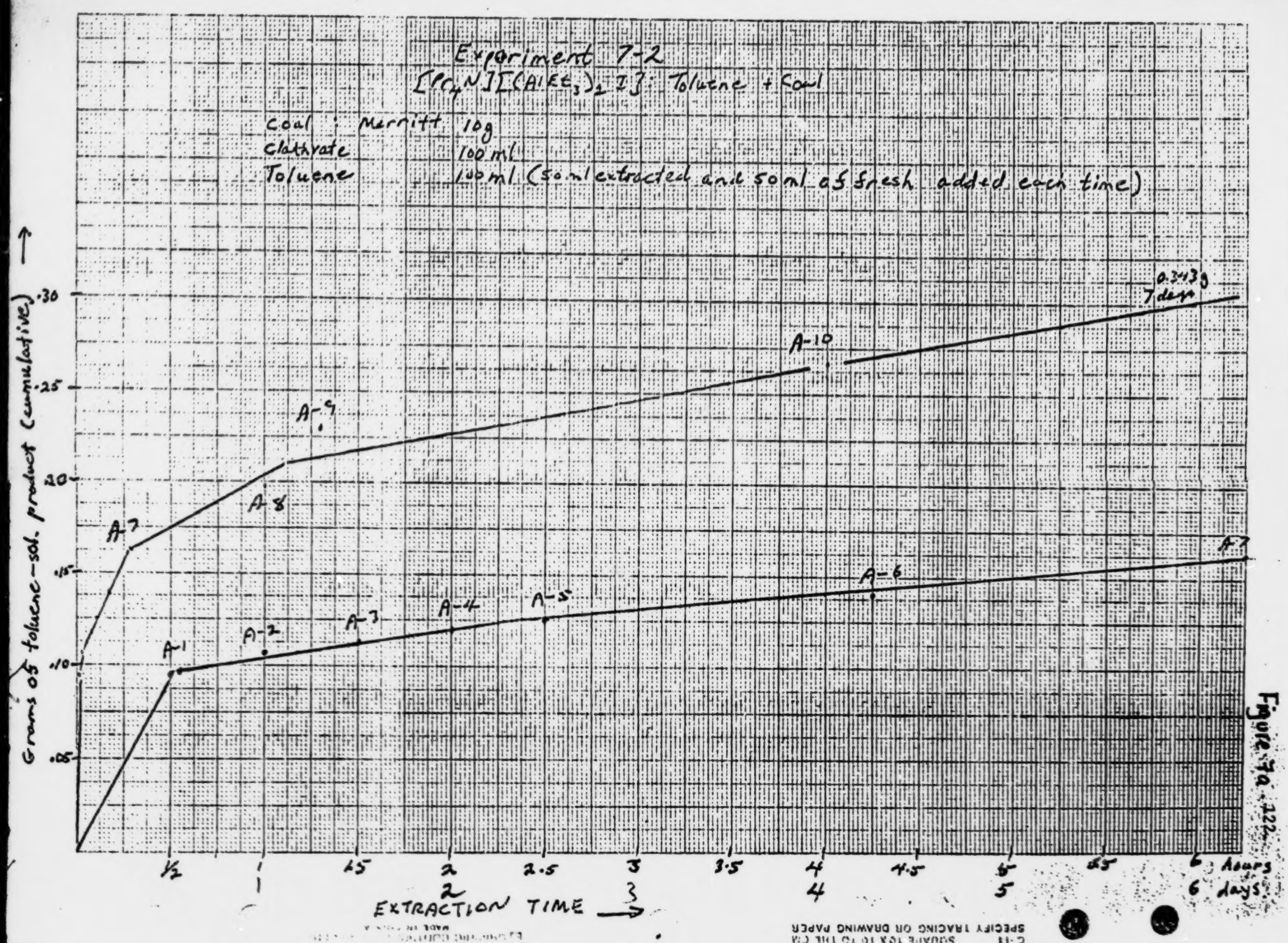
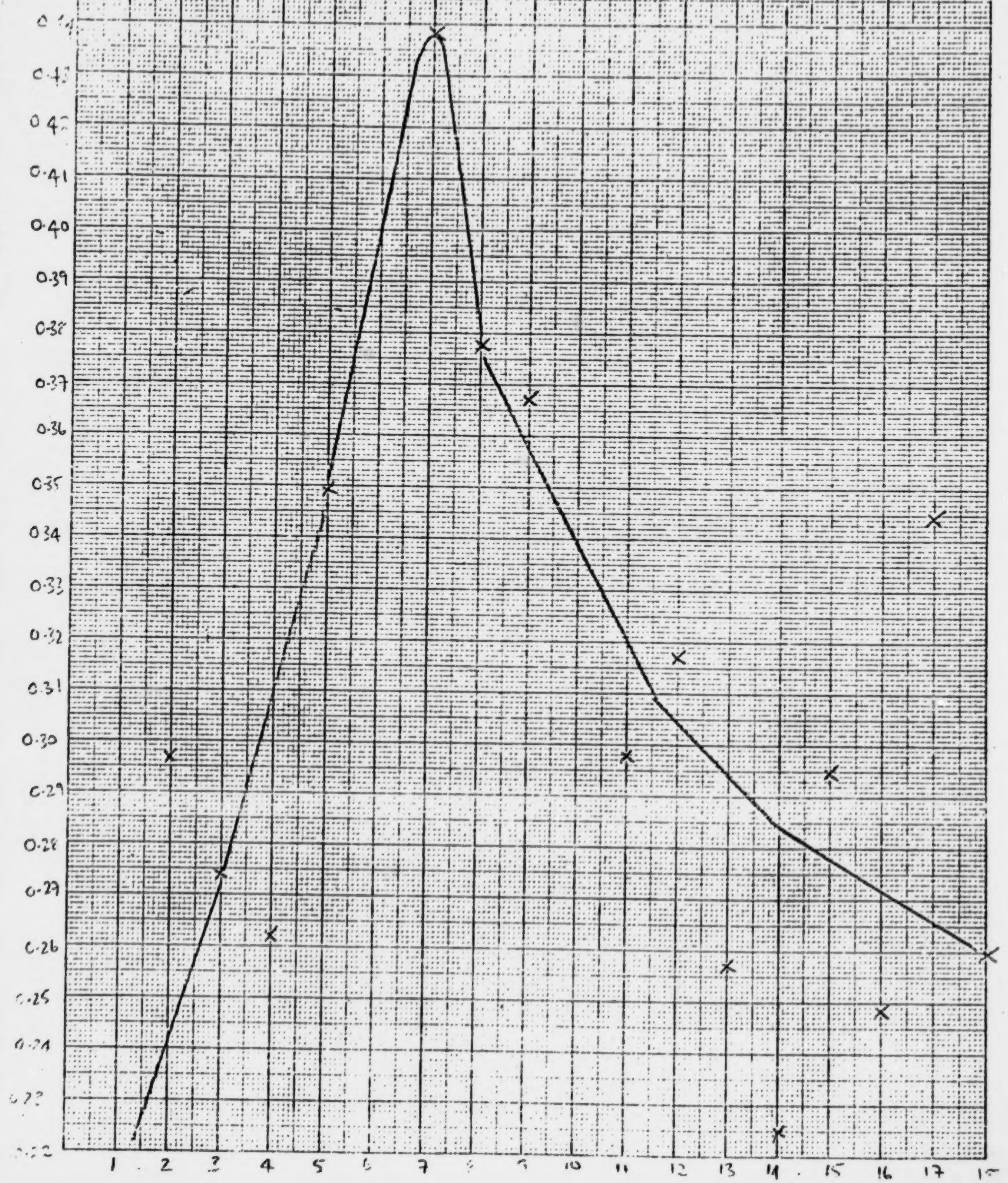

Experiment 7-2
$[Pr_4N][(AlEt_3)_2 I]$: Toluene + Coal
Coal : Merritt 10g
Clathrate 100 ml
Toluene 100 ml (50 ml extracted and 50 ml of fresh added each time)
Grams of toluene-sol. product (cumulative) →
.30
.25
.20
.15
.10
.05
A-7
A-8
A-9
A-10
0.3413g
7 days
A-1
A-2
A-3
A-4
A-5
A-6
A-7
1/2
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6 hours
1
2
3
4
5
6 days
EXTRACTION TIME →
C-11 SQUARE 10 X 10 TO THE CM
SPECIFY TRACING OR DRAWING PAPER

Figure 7a

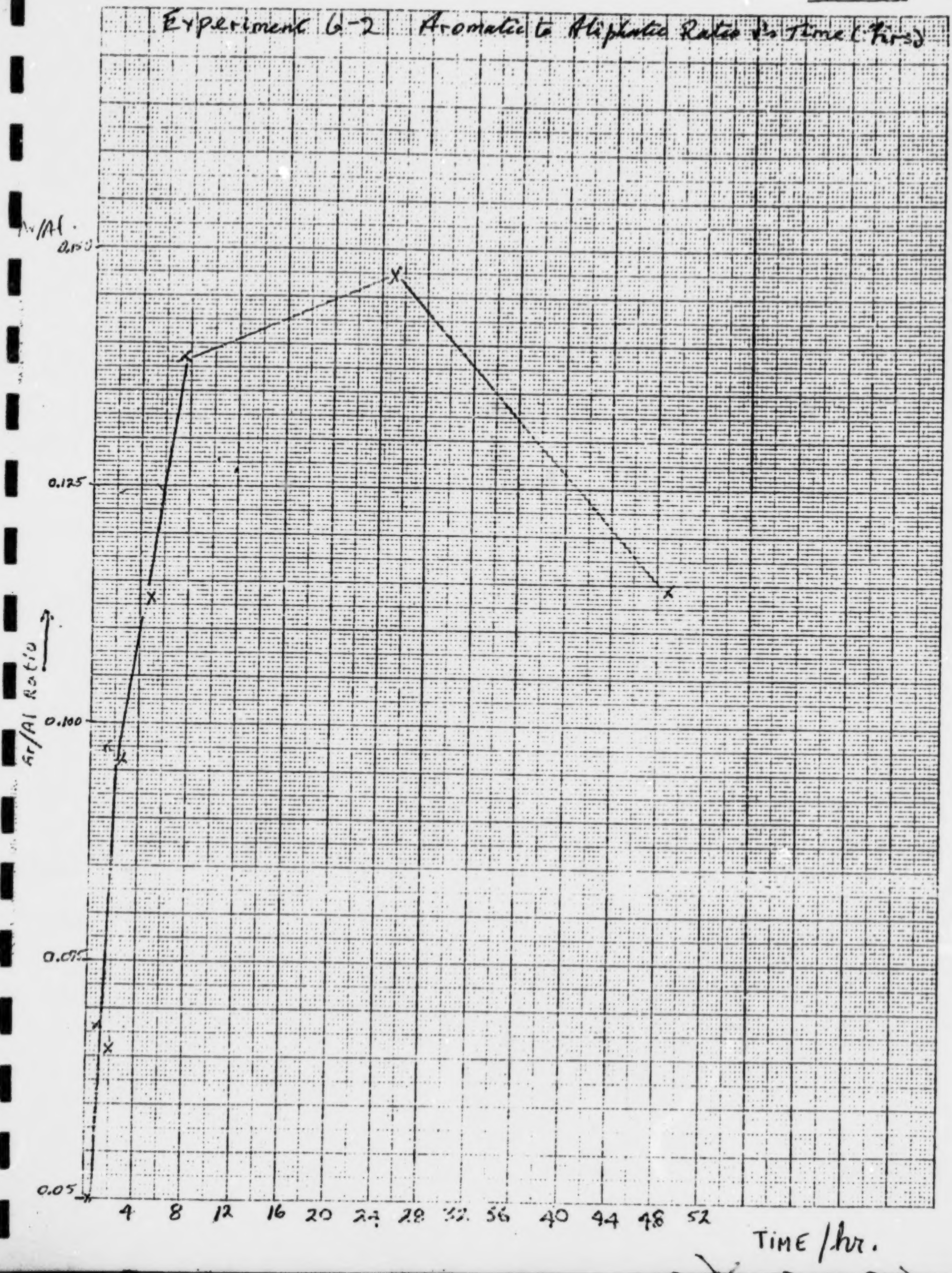
Figure 1.b

Graph showing Aromatic to Aliphatic ratios for successive samples of lithium solubles in experiment 2-9 (Ar/Al obtained from integration of NMR spectra).



2-9A (1-18).

Figure 2. b



Experiment 6-2 Aromatic to Aliphatic Ratio vs Time (First)

APPENDIX II.1.9

REMOVAL OF RESIDUAL PYRIDINE

REMOVAL OF RESIDUAL PYRIDINE

Examination of the pyridine soluble fractions by NMR requires the removal of all traces of pyridine. Several methods have been tried for the removal of the final traces of pyridine, but to date none has proven totally satisfactory and further work is in progress

Pumping on the samples on a vacuum line for 24 hours failed to remove the residual pyridine, as did extensive washing (total volume 1 litre) with pentane. Washing with 5% HCl, followed by water, also failed to remove the pyridine. The samples were mixed with toluene and distilled as the 1:5 pyridine:toluene azeotrope. After such distillation the amount of pyridine was reduced but the samples still contained too much pyridine for satisfactory NMR.

To date the most promising method for removal of the residual pyridine has been the "vacuum pistol" technique for removal of traces of solvents. Small samples were refluxed for 6 - 7 hours with carbon tetrachloride under vacuum. The sample was then weighed into the NMR tube and 0.5 ml of a 1% methylene chloride in pyridine-d_5 solution added as an internal standard. Figure 1 shows the NMR of the calibration solution (1% methylene chloride in pyridine-d_5); Figure 2 shows the NMR of the sample (and standard) prior to treatment in the vacuum pistol; Figure 3 shows the NMR of the sample (and standard) after 6½ hours in the vacuum pistol. Comparison of Figures 2 and 3 indicate an increase in the intensity in the aromatic and aliphatic regions due to the pyridine soluble material, relative to the standard. However, relatively sharp peaks are still observed in the aromatic region and further work is required on the system.

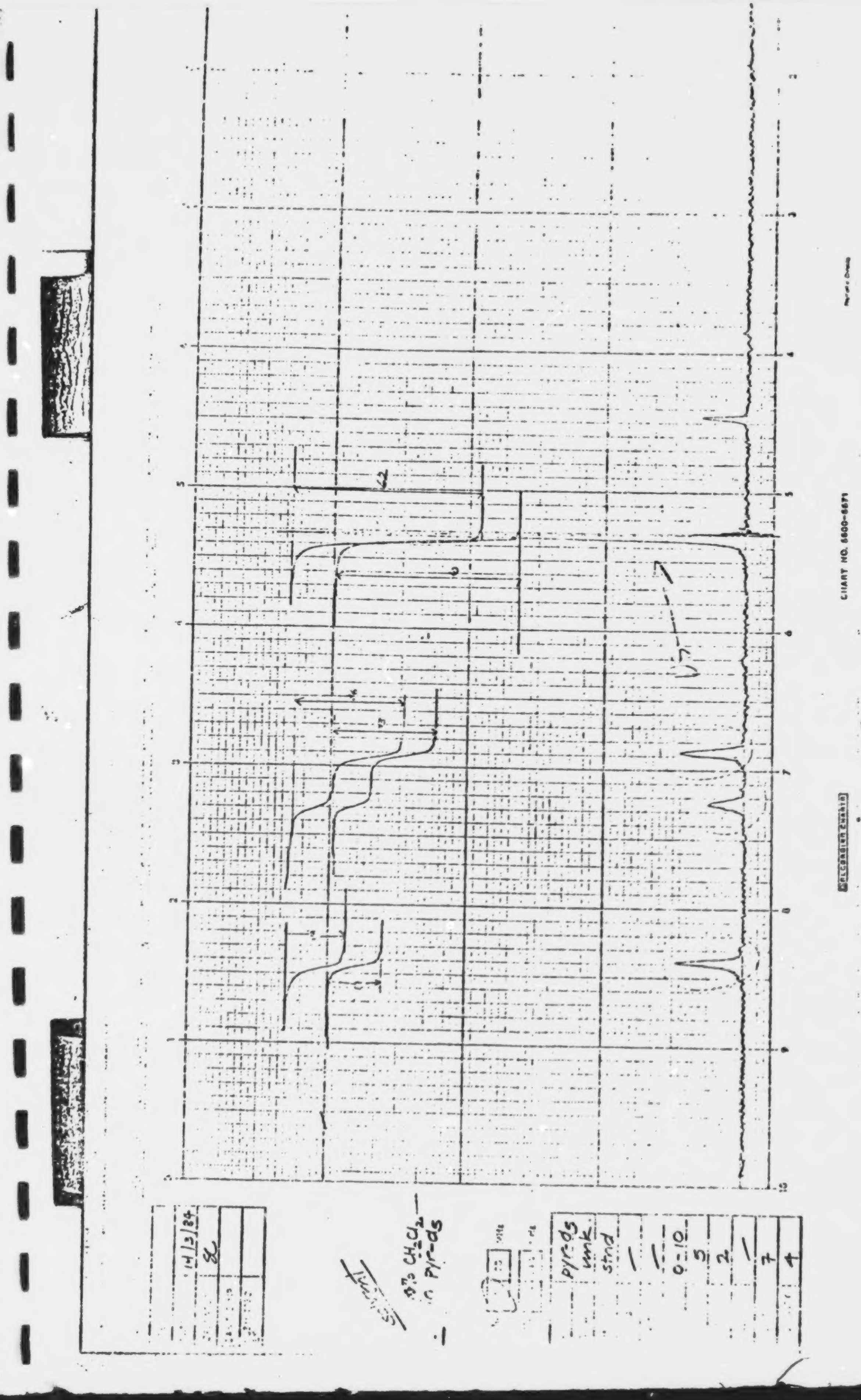


Figure 1

1% Methylene Chloride Standard

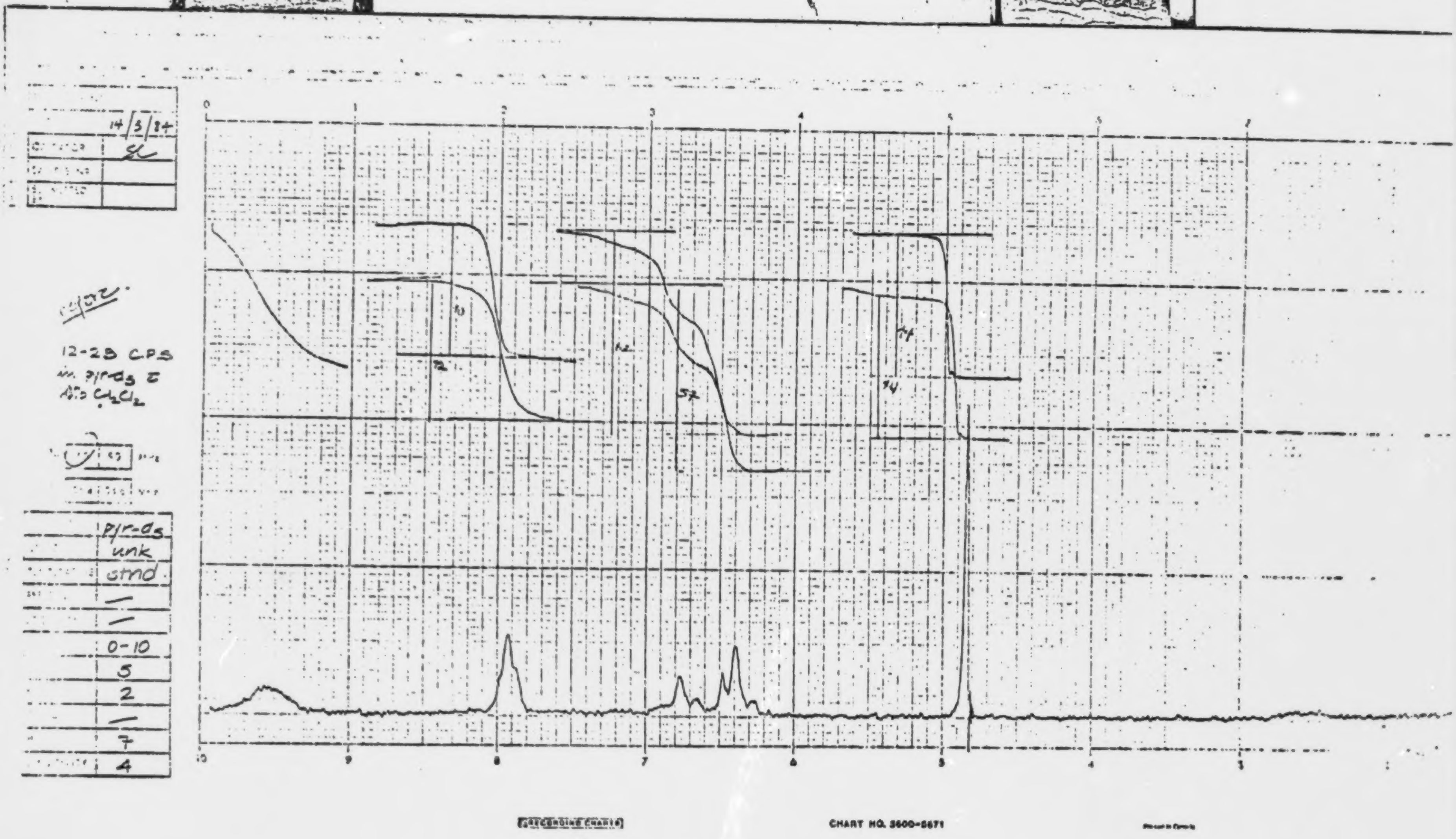


Figure 2

Sample 12-28 - pyridine solubles + 1% methylene chloride
Before treatment in vacuum pistol.

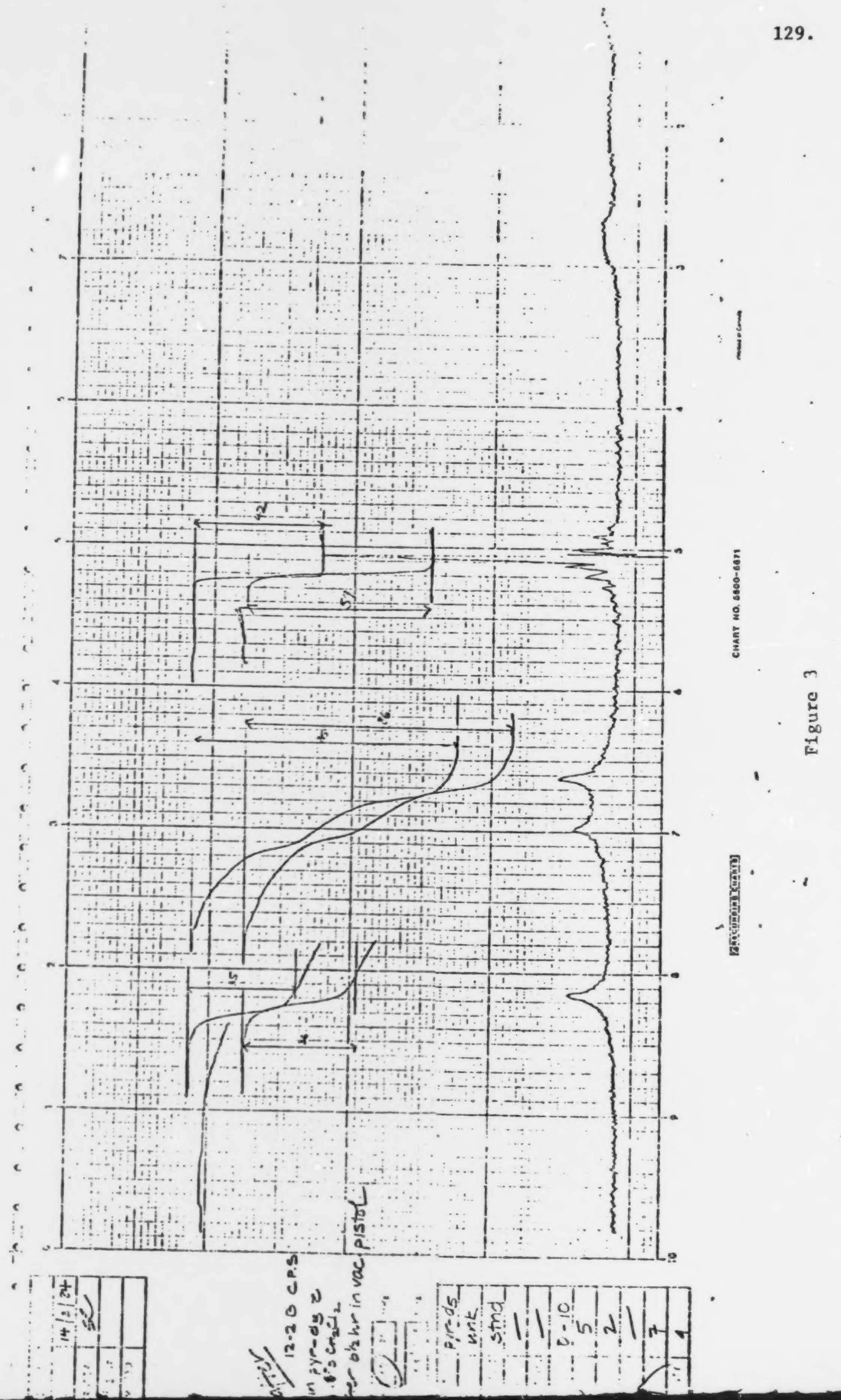


Figure 3

Sample 12-28 +standard - after 6½ hours in vacuum pistol.

APPENDIX II.1.10

^{1}H NMR SPECTRA OF CLATHRATES

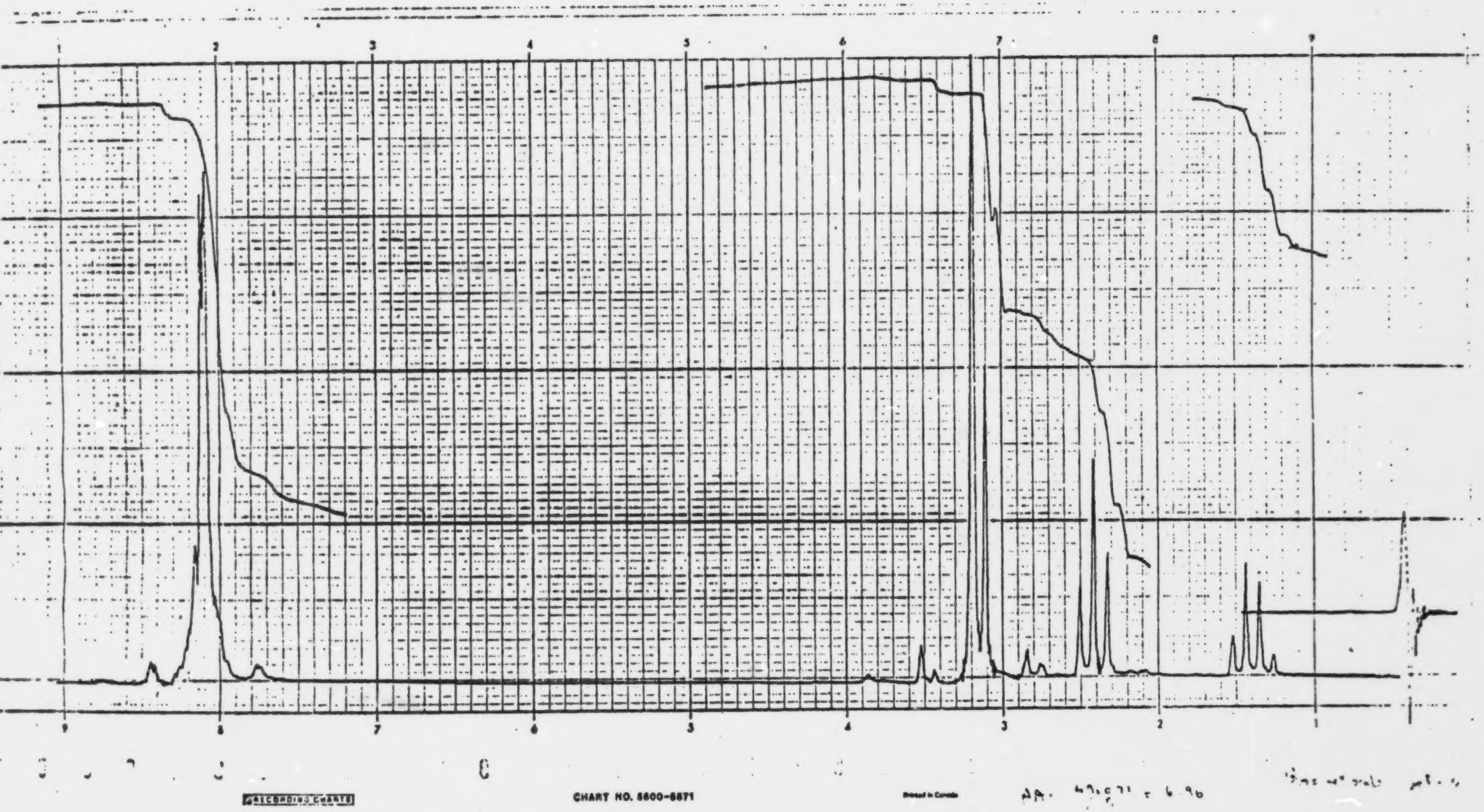


Figure 1. ¹H N.M.R. (90MHz) of $[NMe_4][Al_2Et_6I]$.toluene liquid clathrate

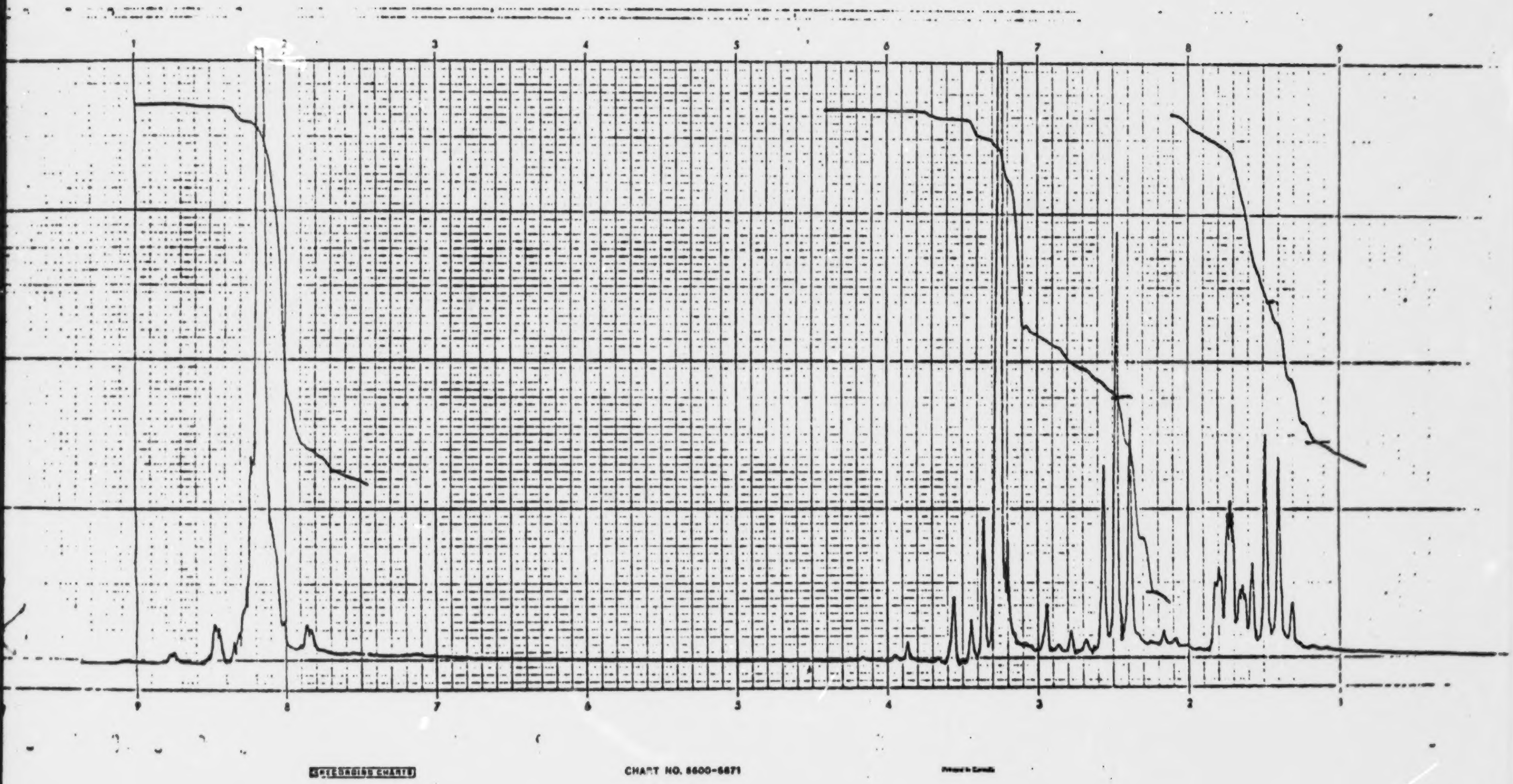


Figure 2 ^{1}H N.M.R. (90MHz) of $[NEt_4][Al_2Et_6I]$.toluene liquid clathrate

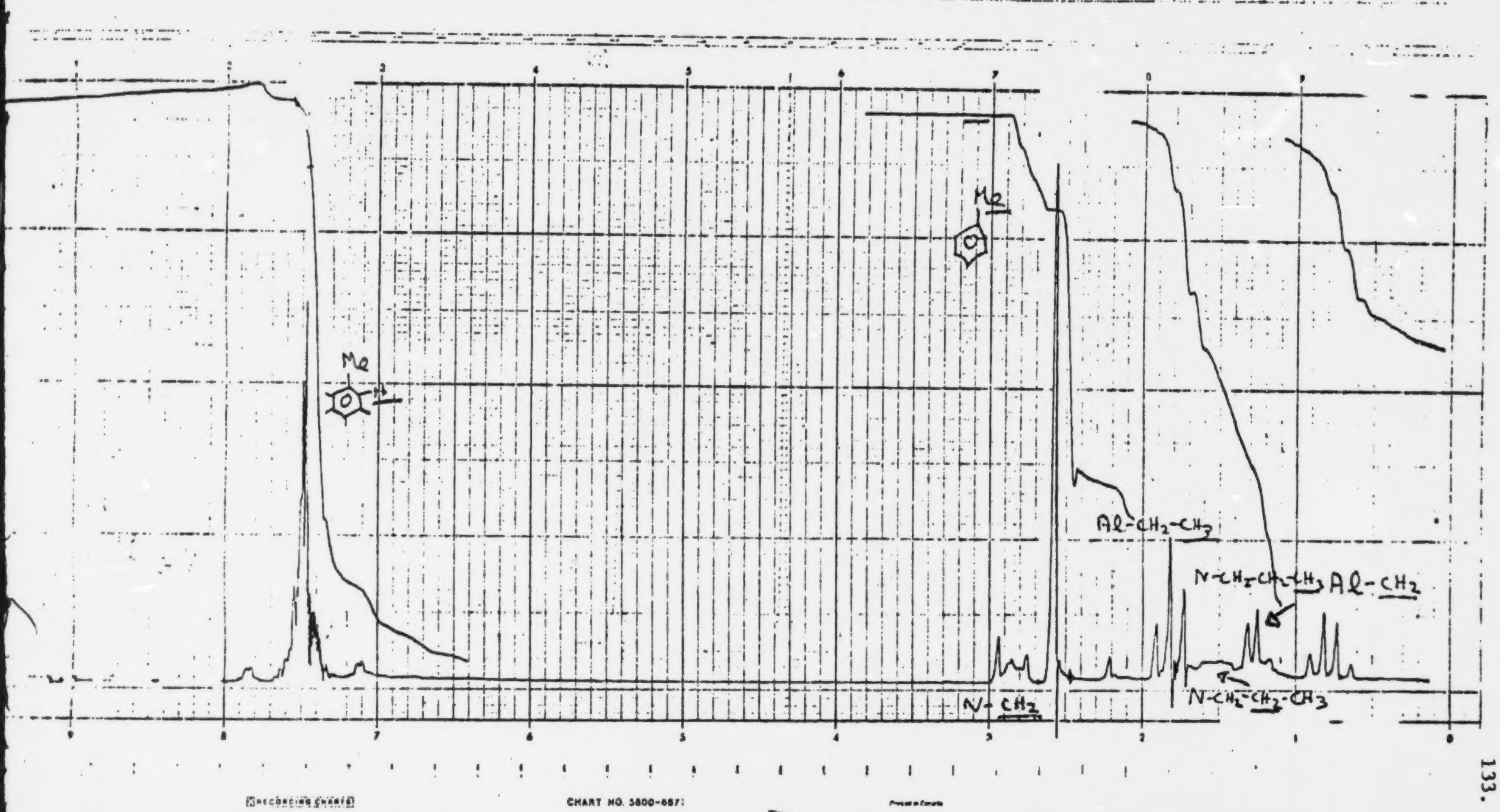


Figure 3 ¹H N.M.R. (90MHz) of $[NPr_4][Al_2Et_6I]$. toluene liquid clathrate

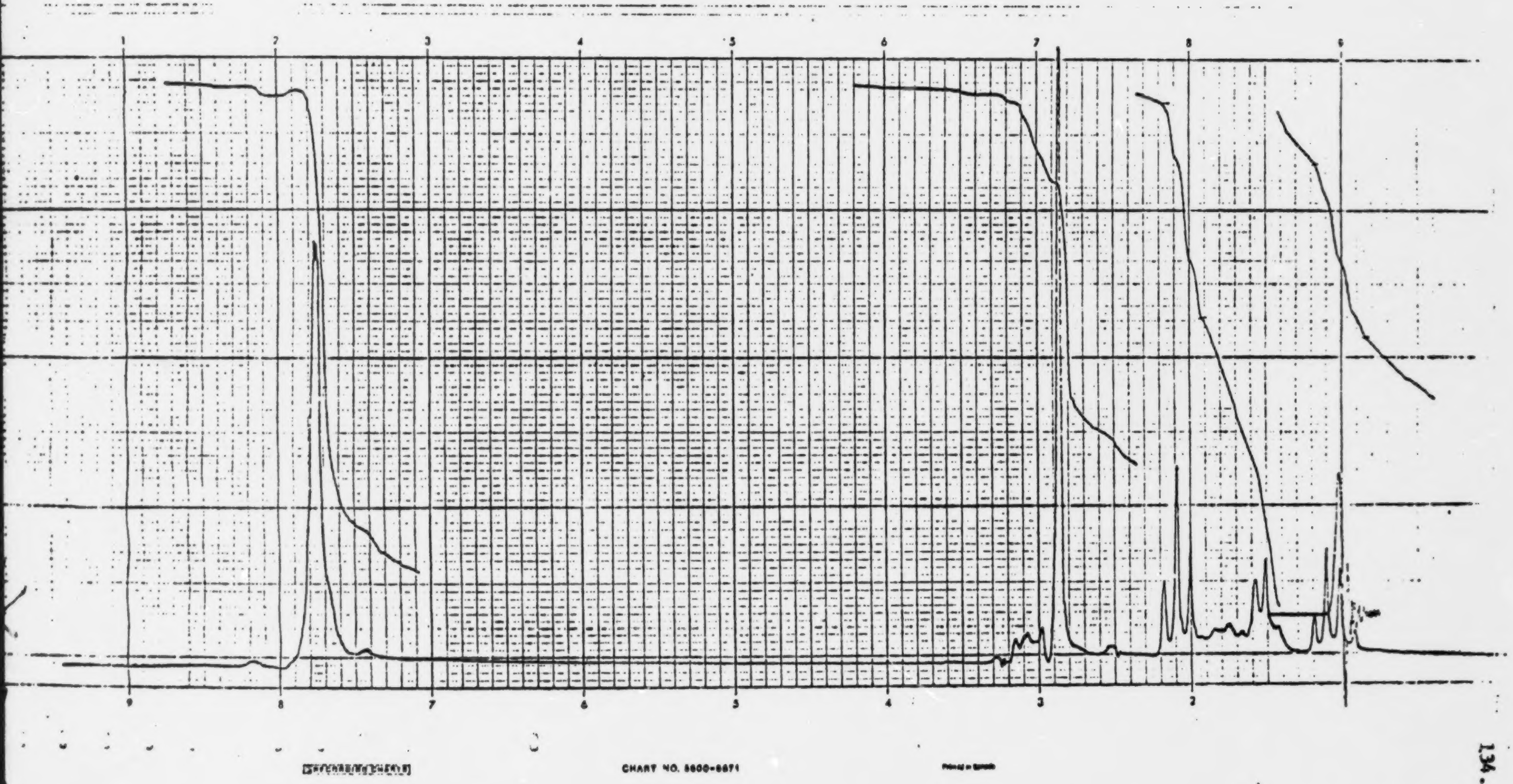


Figure 4. 'H N.M.R. (90MHz) of [NBu$_4$][Al$_2$Et$_6$I].toluene liquid clathrate.

APPENDIX II.1.11

CHARACTERISATION OF TOLUENE SOLUBLE LIQUID CLATHRATE DERIVATIVES

CHARACTERISATION OF TOLUENE SOLUBLE LIQUID CLATHRATE DERIVATIVES

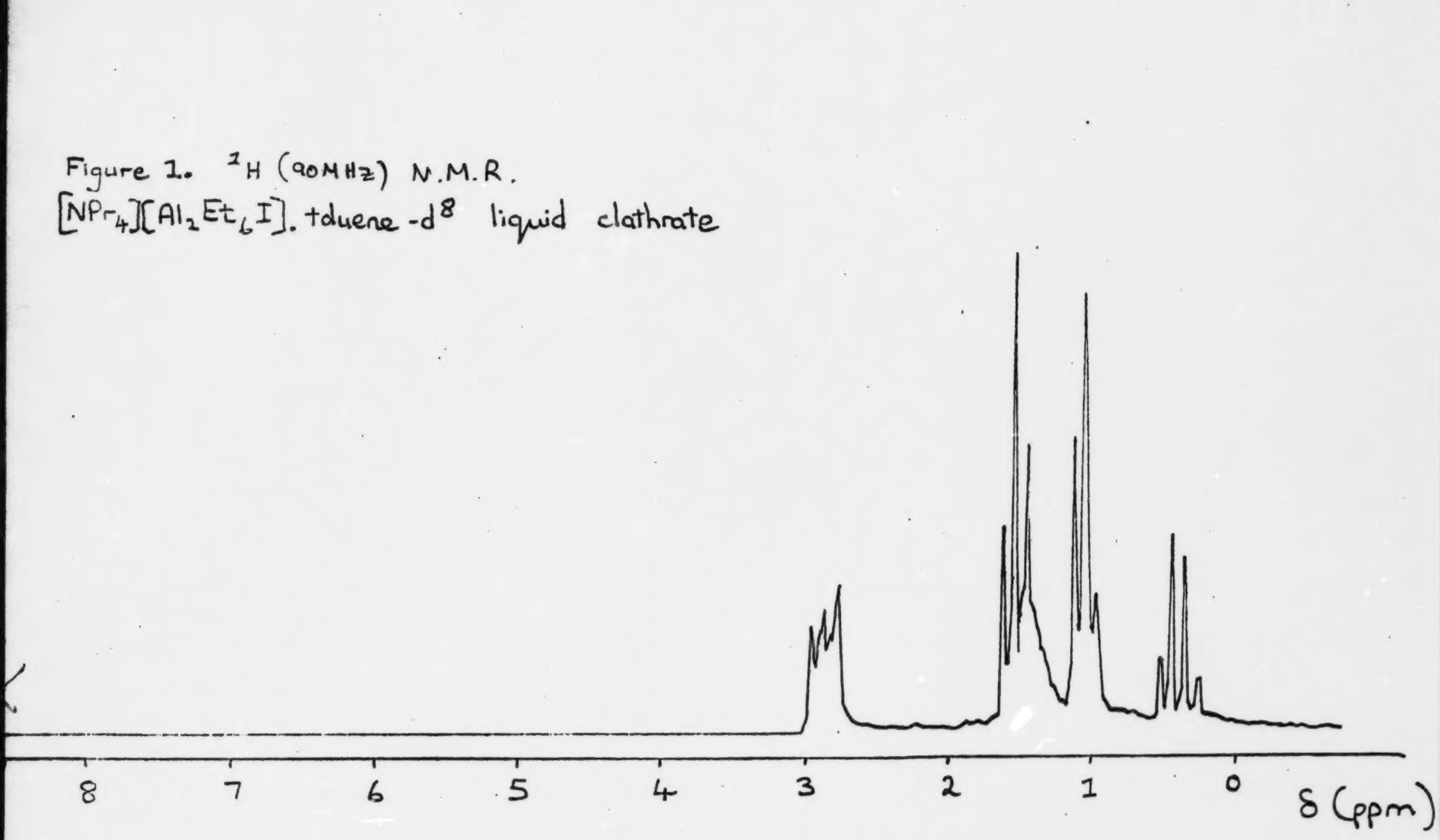
The nature of the ineractions occuring between the coal, the clathrate and the toluene will be investigated in Phase II. However, some preliminary investigations have been conducted in Phase I using toluene-d_8 so that ^1H NMR spectra of the toluene soluble species could be observed directly.

3.44 g of NPr_4I (11.0 mmole), 3.00 ml of $AlEt_3$ (22.0 mmole) and 25 g of toluene-d_8 were mixed together in an inert atmosphere glove box. Approximately 15 ml of liquid clathrate formed within five minutes, dissolving completely the NPr_4I in the process. A 90 MHZ proton NMR of the liquid clathrate is presented in Figure 1, and is identical (apart from the absence of toluene signals) with the spectrum of the analogous toluene based liquid clathrate (Appendix II.1.1). 10 ml of the toluene-d_8 liquid clathrate was used along with 10 ml of toluene-d_8 to extract 1.00 g of K seam coal in the normal manner (18 hr., 70°C). The system was allowed to form two phases following the reaction, and proton NMR spectra were obtained of each phase. The lower (liquid clathrate) layer, although now black in colour, gave an NMR identical to that of the unreacted liquid clathrate (Figure 2). The upper (toluene-d_8) layer gave a spectrum consistent with the presence of a small amount of NPr_4I and a larger amount of hitherto new material (Figure 3). Further work is required before a conclusion may be reached regarding the nature of the material, but the spectrum shows resonances consistent with the presence of both Al-Et linkages. Aluminoxane compounds of the type previously identified by Atwood (1,2) as liquid clathrate derivatives are thus the most likely form of the toluene soluble liquid clathrate derivatives.

1. Atwood, J.L.; Hrincir, D.C.; Priester, R.D.; Rogers,R.D. Organometallics, 2, 985 (1983).

2. Atwood, J.L.; Zaworotko, M.J.; Chemical Commun, 302 (1983).

Figure 1. ^1H (90MHz) N.M.R.
$[NPr_4][Al_2Et_6I]$. toluene-d^8 liquid clathrate



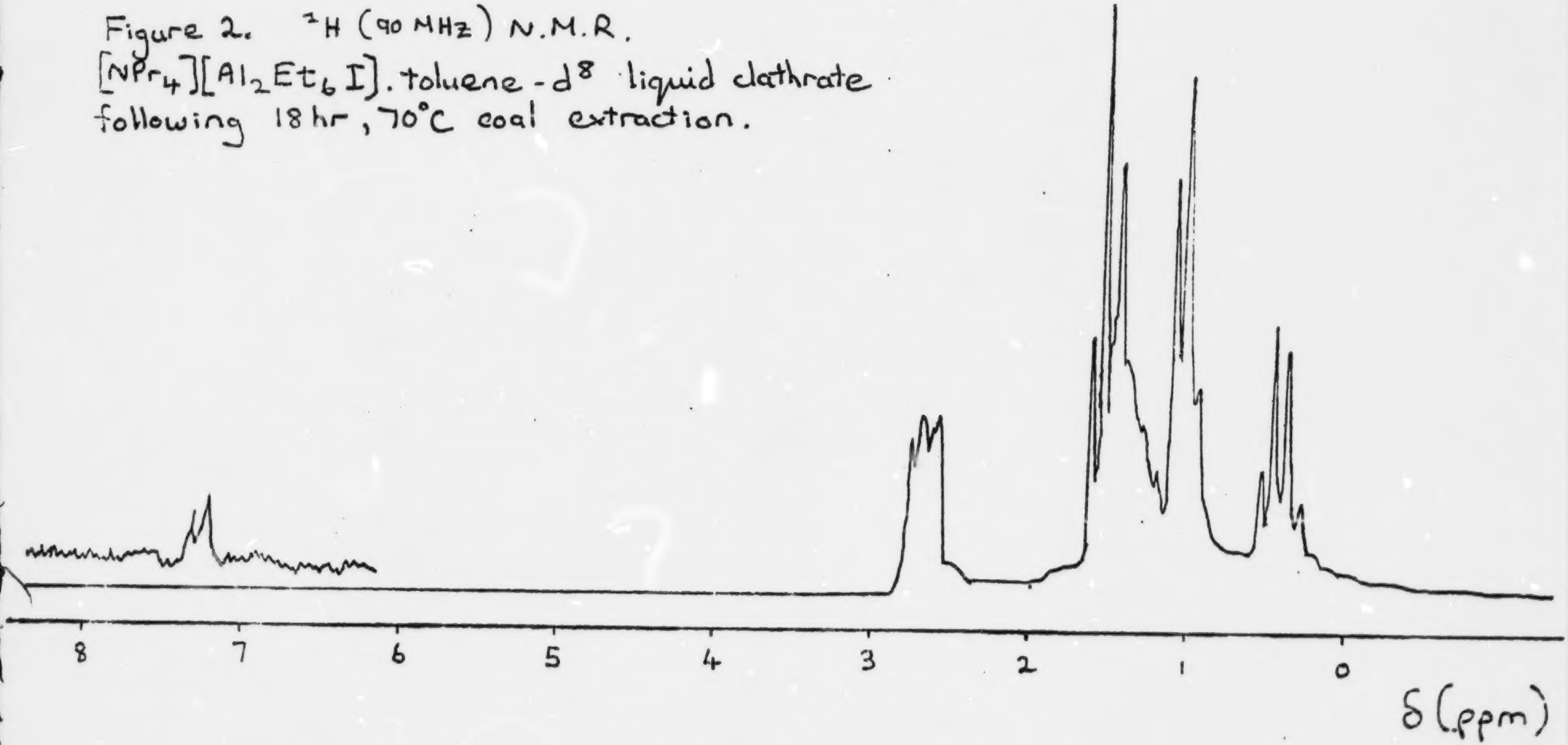


Figure 2. ^2H (90 MHz) N.M.R.
$[NPr_4][Al_2Et_6I]$. toluene-d^8 liquid clathrate following 18 hr, 70°C coal extraction.

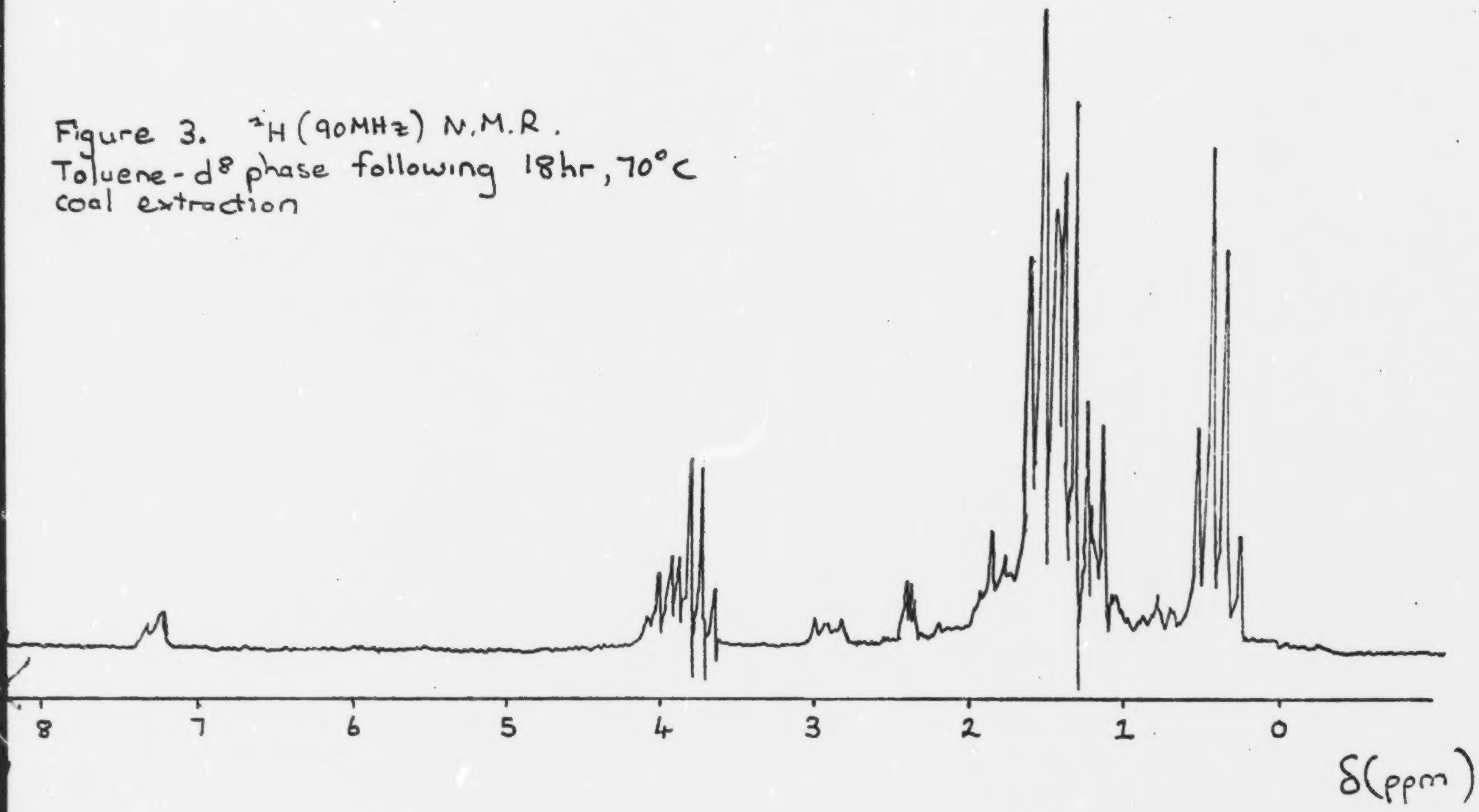


Figure 3. ^{2}H (90MHz) N.M.R.
Toluene-d^{8} phase following 18hr, 70°C coal extraction

APPENDIX II.1.12

a) SOXHLET EXTRACTION OF COAL

b) REFLUX EXTRACTION OF COAL

a. SOXHLET EXTRACTION OF COAL

A clean, dry, labelled 250 ml round bottom flask was preweighed on the top-loading balance to 3 decimal places. The flask was clamped to a support stand in a fumehood. A thimble with residue was placed into a a soxhlet extractor which was attached to the flask and clamped.

Cooling water was passed through a pressure regulator to a Graham Condenser on the soxhlet extractor. A 250 ml heating mantle, supported by an iron ring was placed under the round bottom flask and the mantle plugged into a 1.4 KVA voltage regulator set at 90. 150 ml of dry distilled toluene was poured into the round bottom flask.

A Pasteur pipette was placed, well down into the solvent, through the sidearm of the flask. A nitrogen bleed was attached to the pipette, (the nitrogen was passed through an H_2SO_4/KOH scrub beforehand) and heating begun.

After approximately one-half hour the soxhlet was checked. The extract varied in colour from pale yellow to dark brown. The nitrogen bleed was kept bubbling steadily but not violently.

Extraction was continued for 17 hours (overnight).

After extraction the heating mantle was turned off, removed and the flask allowed to cool in position. The condenser was removed and the soxhlet thimble lifted and clamped above the level of the solvent. It was allowed to drain for approximately 10 minutes. The soxhlet thimble was placed in a labelled 250 ml beaker in the back of the fumehood to dry for a day.

The solvent was drained from the soxhlet extractor into the round bottom flask. The extractor was rinsed with about 20 ml of clean, dry toluene which was transferred into the round bottom flask. This procedure was repeated. The nitrogen bleed was disconnected, and the Pasteur pipette changed to one with a drawn-out end. The solvent was vacuum distilled as in Appendix II.1.7.

The flask with label was re-weighed to 3 decimal places. The residue in the round bottom flask was transferred to a 6 dram snap-cap storage vial using about 5 ml total of $CDCl_3$ (without TMS). The vial was stored in the freezer.

When the soxhlet thimble was dry, it was placed in a 10 cm glass powder funnel. The stem of the funnel was placed in the mouth of a 1 litre Erlenmeyer flask. 500 ml of de-ionized water was filtered through the soxhlet thimble, over a number of hours and the filtrate was discarded. The thimble was allowed to dry for several hours then placed in a beaker in a vacuum oven. The thimble was heated under vacuum at 80°C overnight. The thimble was either cooled under vacuum in the vacuum oven or quickly transferred to a dessicator to cool. Once cool, it was weighed to 4 decimal places.

The pyridine soxhlet was prepared as described above, but using dry distilled pyridine. Pyridine contents were black in colour. The soxhlet thimble was not washed with water and was dried in the fumehood, then in the vacuum oven.

b. REFLUX EXTRACTION OF COAL

10 g of 100 mesh vacuum oven-dried coal was weighed into a clean, dry 250 ml one neck round bottom flask. 150 ml of distilled solvent was added (either toluene, $CHCl_3$ or pyridine). The flask was clamped onto a support stand and a water-cooled condenser was placed in the top. A 250 ml heating mantle was placed under the flask and plugged into a 1.4 KVA voltage regulator which was set at 60 (for toluene and pyridine). The extractions were continued for 17 hours (overnight).

The flask was allowed to cool. A Pasteur pipette was filled with solvent several times and the inside walls of the condenser rinsed. The solution was poured through a dry pre-weighed soxhlet thimble to remove the coal. The flask was rinsed several times to remove all the coal residue. The thimble was dried in the fumehood overnight, then placed in a vacuum oven for complete drying. The solution was placed in a clean, dry, pre-weighed 250 ml 2 neck flask and vacuum distilled as described in Appendix II.1.7.

APPENDIX II.1.13

^{1}H NUCLEAR MAGNETIC RESONANCE SPECTRA

Figure 1. Sample 2-30-A1

Continuous extraction experiment. Toluene soluble material that collected in reflux flask.

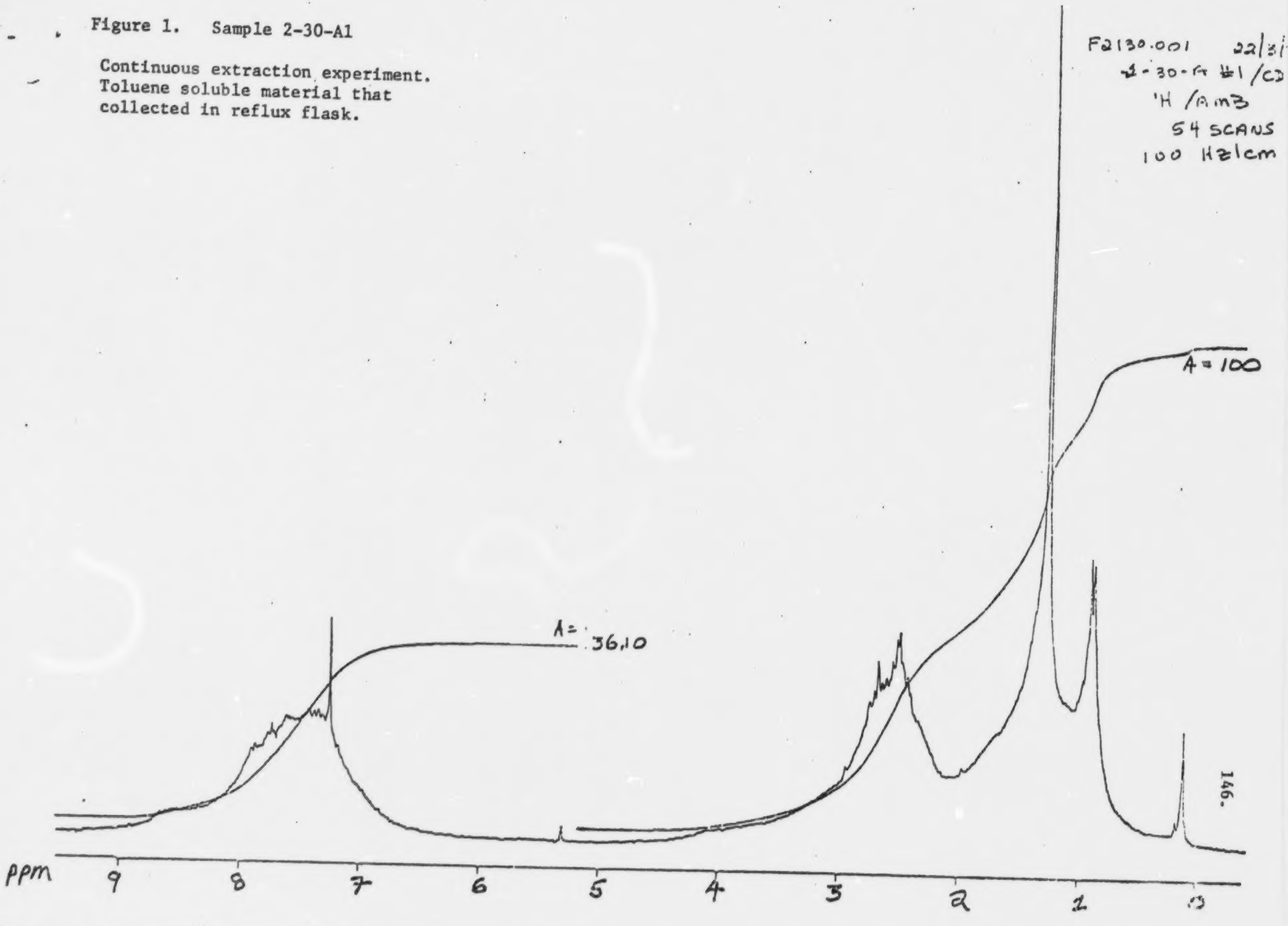


Figure 2. Sample 2-30 A2

Continuous extraction experiment.
Toluene soluble material that was
in contact with the coal and clathrate
phases at the end of the experiment.

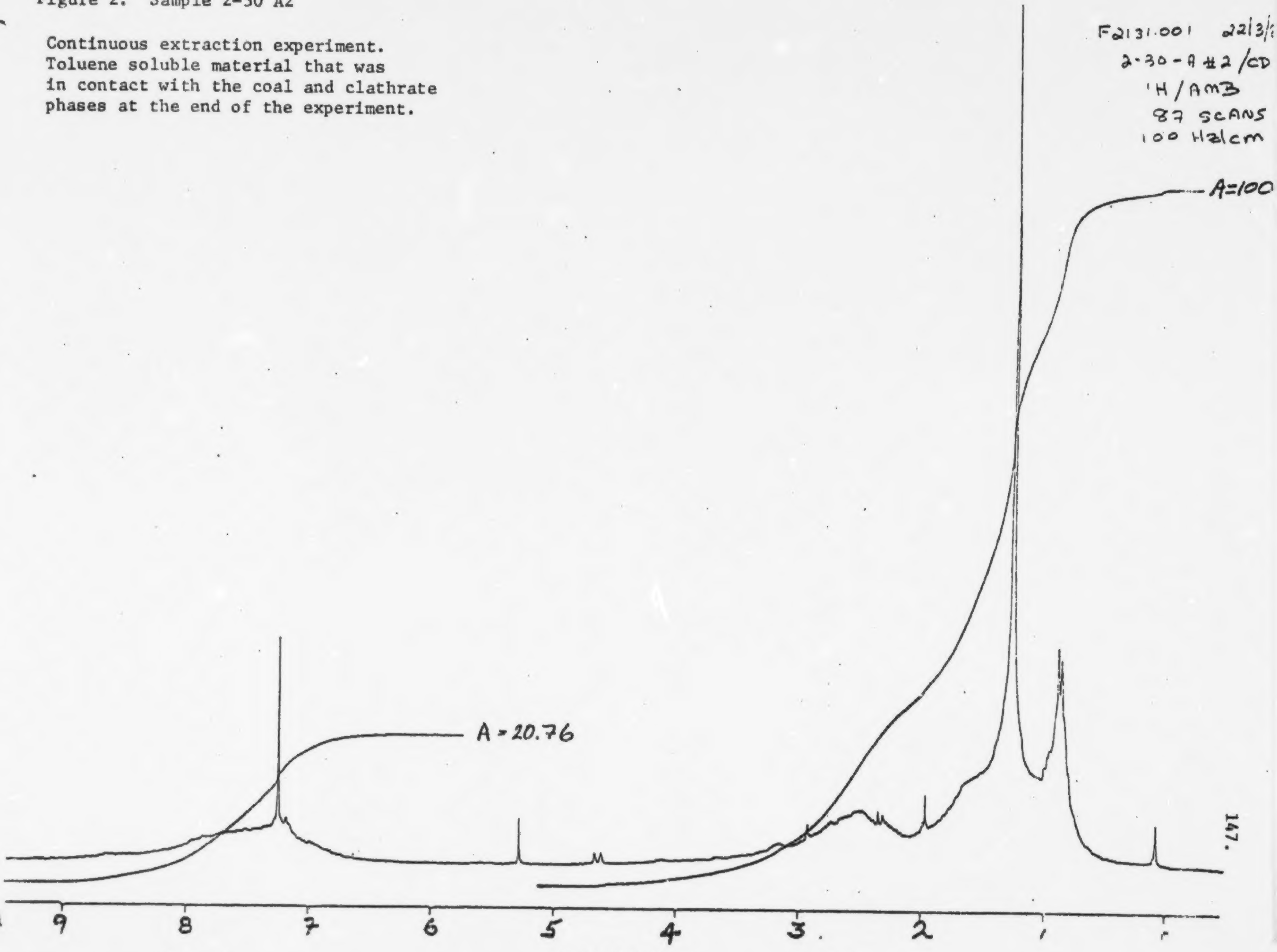
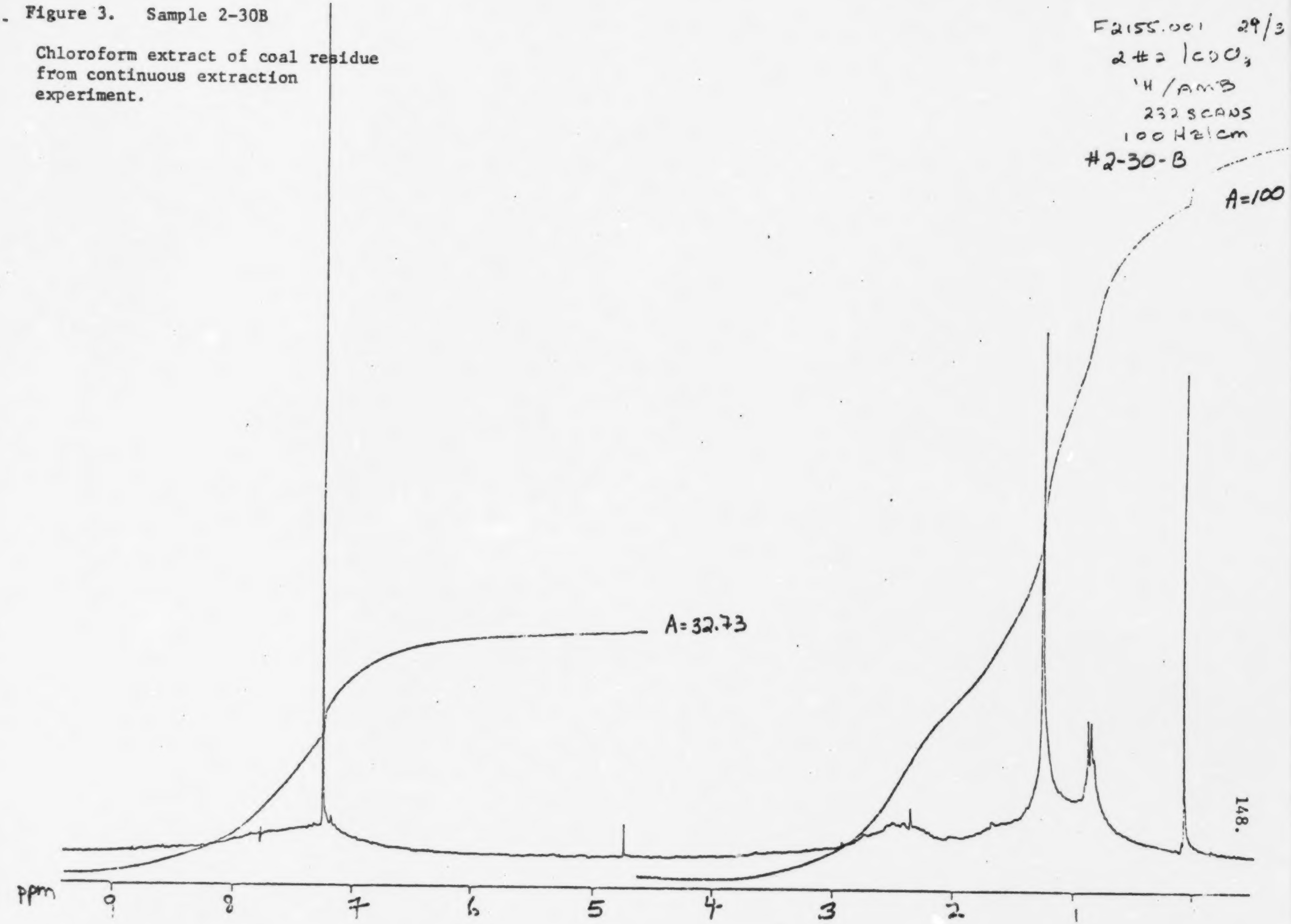


Figure 3. Sample 2-30B

Chloroform extract of coal residue from continuous extraction experiment.



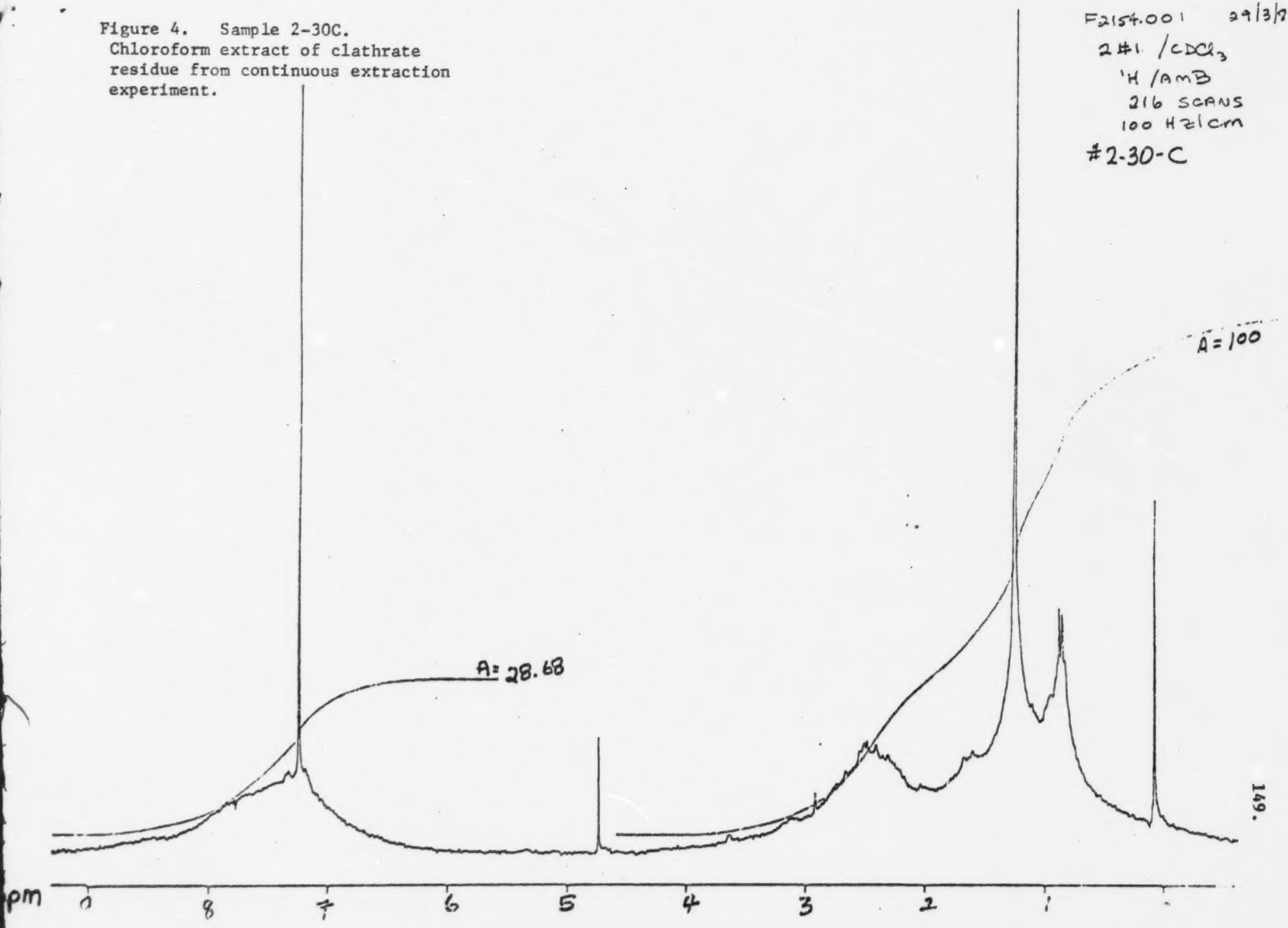


Figure 4. Sample 2-30C.
Chloroform extract of clathrate residue from continuous extraction experiment.

F2154.001 29/3/74
2#1 /CDCl₃
¹H /AMB
216 SCANS
100 Hz/cm
#2-30-C

Figure 5. Sample 2-28 A1

Continuous extraction experiment.
Toluene soluble material that
collected in the reflux flask.

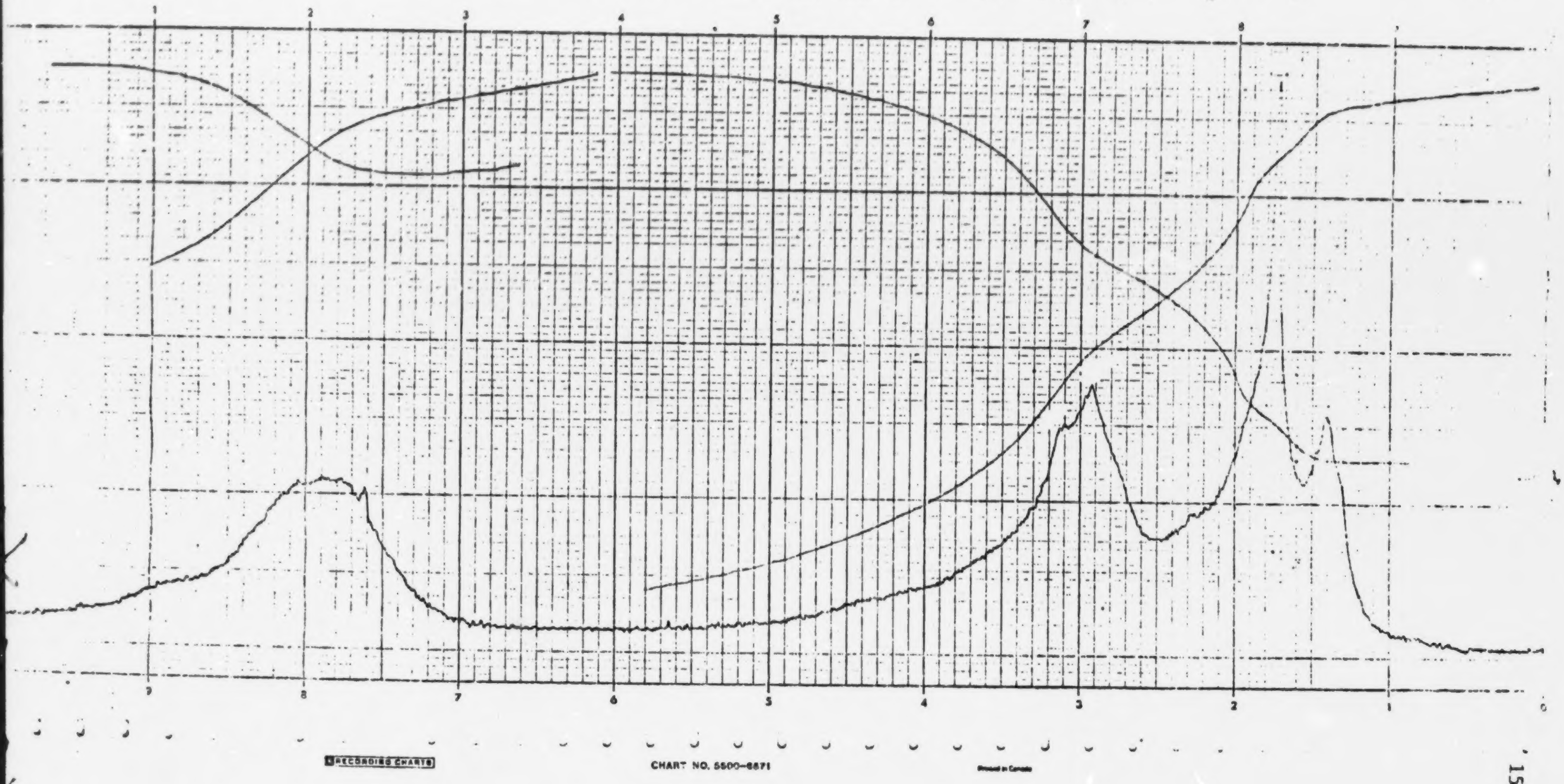


Figure 6. Sample 2-28 A2

Continuous extraction experiment. Toluene soluble material that was in contact with the coal and clathrate phases at the end of the experiment.

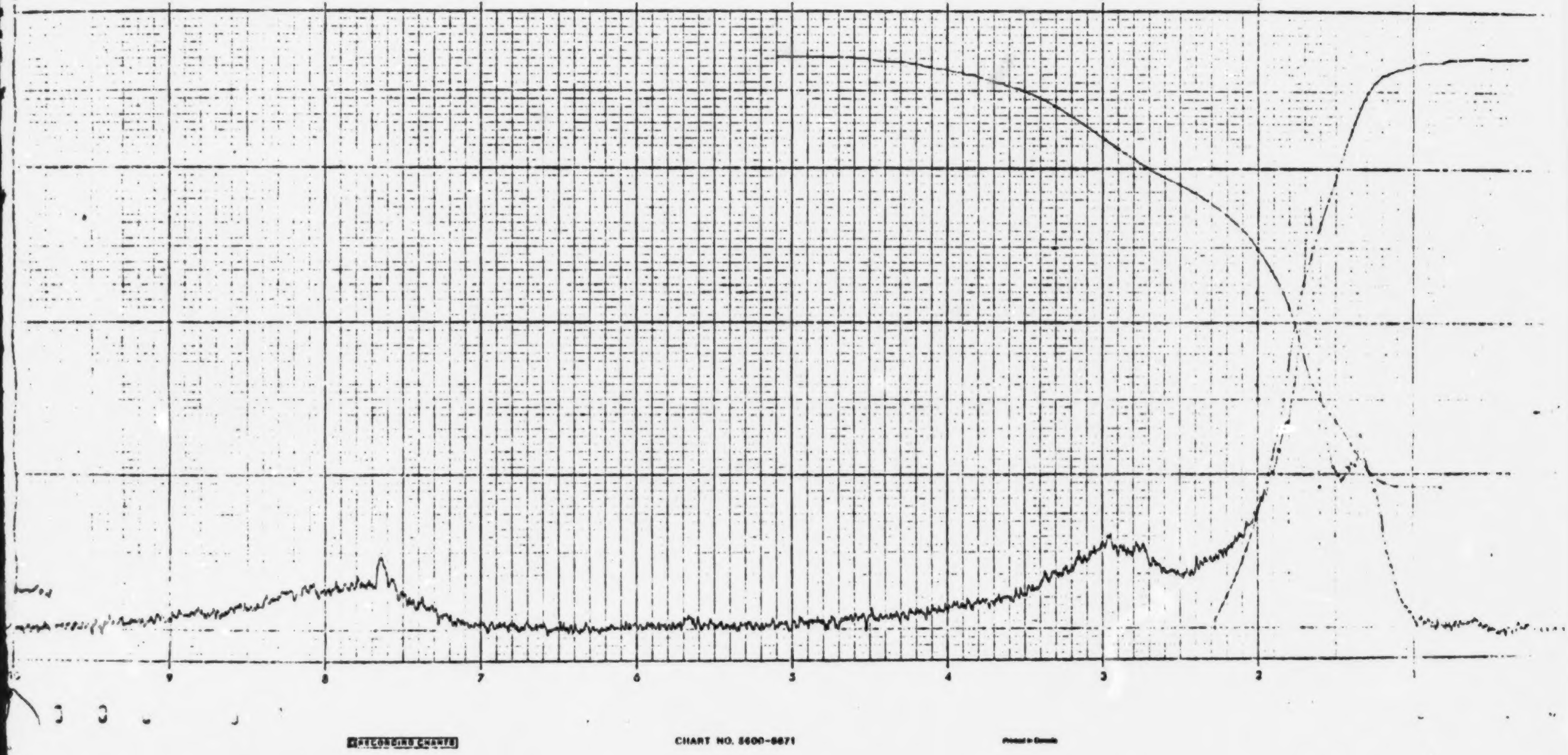


Figure 7. Sample 2-28B

Chloroform extract of coal residue
from continuous extraction experiment.

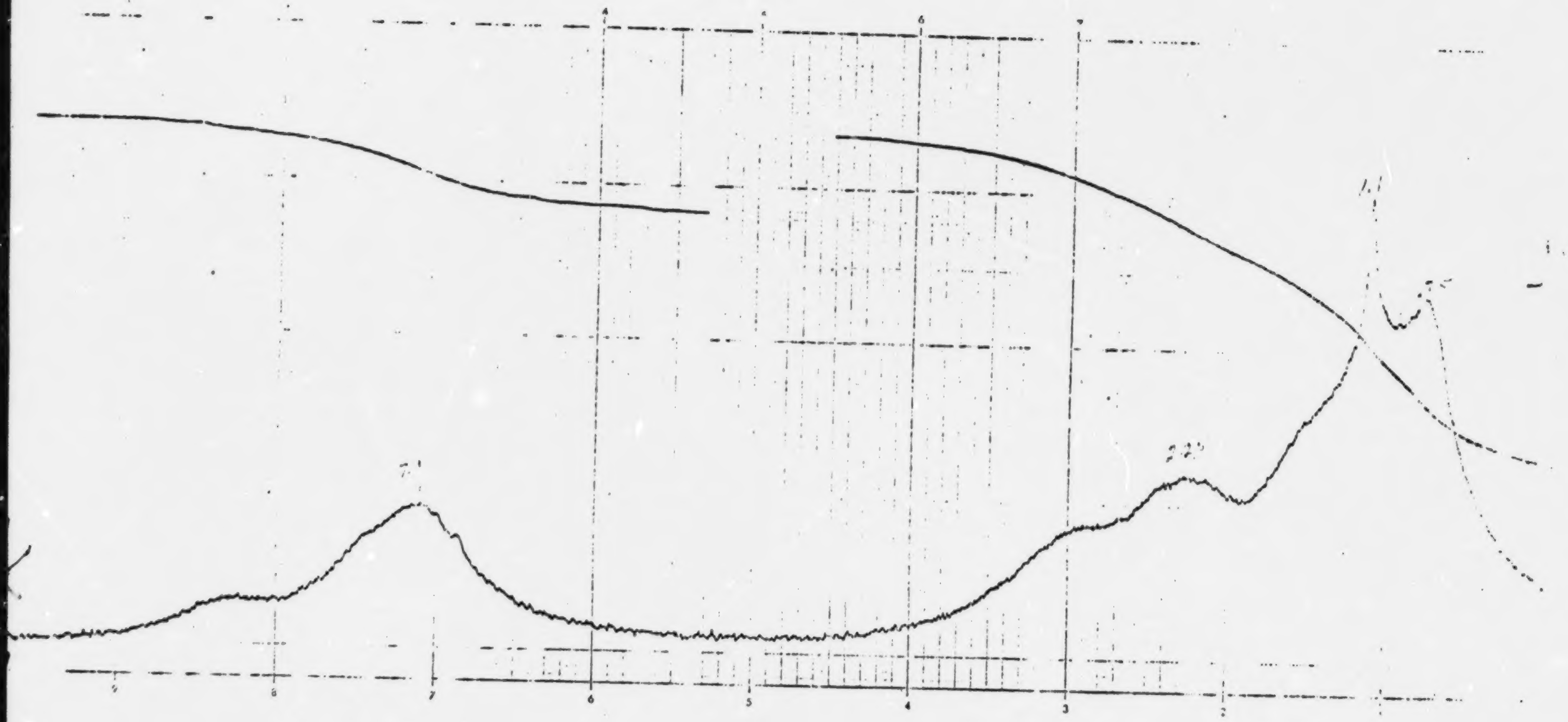
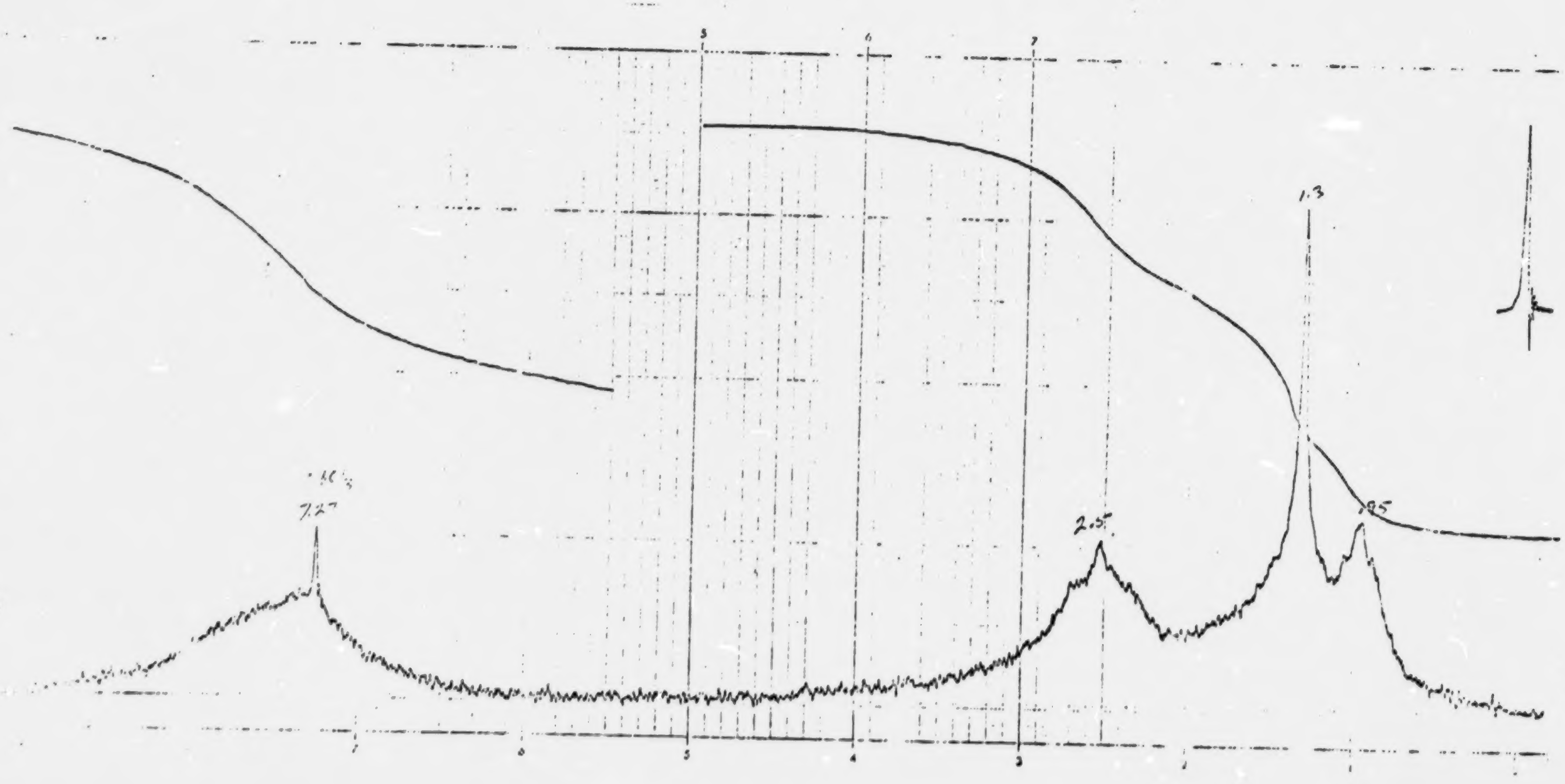


Figure 8. Sample 2-28C

Chloroform extract of clathrate residue from continuous extraction experiment.



APPENDIX II.1.14

MEASUREMENT OF LOSS ON IGNITION

MEASUREMENT OF LOSS ON IGNITION

Porcelain crucibles were ignited at 550°C for 1 hour, allowed to cool in a dessicator and weighed. Suitable amounts of sample were added to the crucibles and the weights recorded again to determine the amount of sample added to each. The crucibles were put into the pre-heated electric muffle furnace and ignited at 550°C for 1.5 hours. They were then placed in the dessicator, allowed to cool to room temperature and weighed again. The % ash and loss on ignition were then calculated. Watch glasses were placed over the crucibles when they were placed in the dessicator, so that the ash would not blow out when the cooled dessicator was opened with the accompanying rush of air.

APPENDIX II.2.1

COAL PREPARATION

COAL PREPARATION

The coal was usually received in a bag or can as an unground sample with both chunks and fines. Sometimes samples were received ground to pass a specific mesh size.

If unground, the coal was broken into small pieces and portions were placed in Moulinex electric coffee grinder. The coal was ground and then passed through a 100 mesh sieve into a 400 ml beaker. This procedure was repeated until all the coal passed the 100 mesh sieve. Usually there were harder pieces remaining near the end which had to be hand ground using an agate mortar and pestle.

Depending on quantity of coal, it was either left in the beaker or spread in a crystallizing dish to a depth of no more than 1 inch. The container with the coal was labelled and the top covered with a filter paper and secured with an elastic band. The coal was dried at 80°C overnight in the vacuum oven.

After drying, the coal was stored in a dessicator charged with an active drying agent.

APPENDIX II.3.1

SCHEMES FOR FRACTIONATION AND ANALYSIS OF COAL LIQUIDS

Figure 1. ANALYTICAL SCHEME FOR WHOLE COAL LIQUID PRODUCT

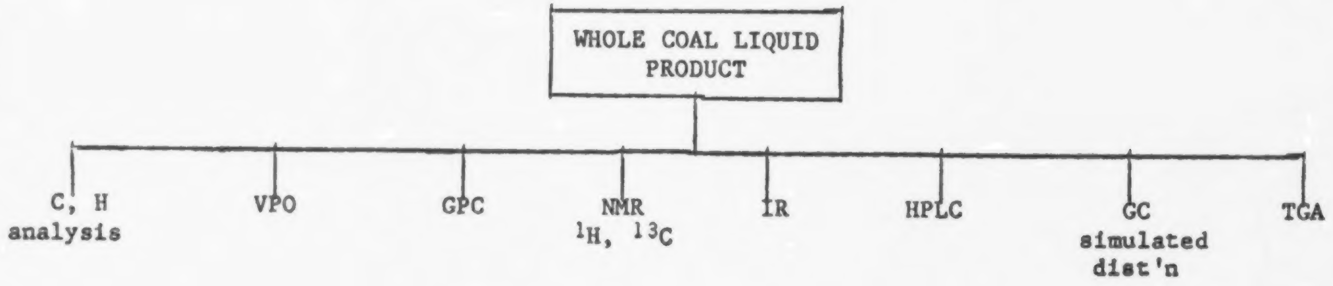


Figure 2. ANALYTICAL SCHEME FOR COLLECTOR SOLUBLE PRODUCT

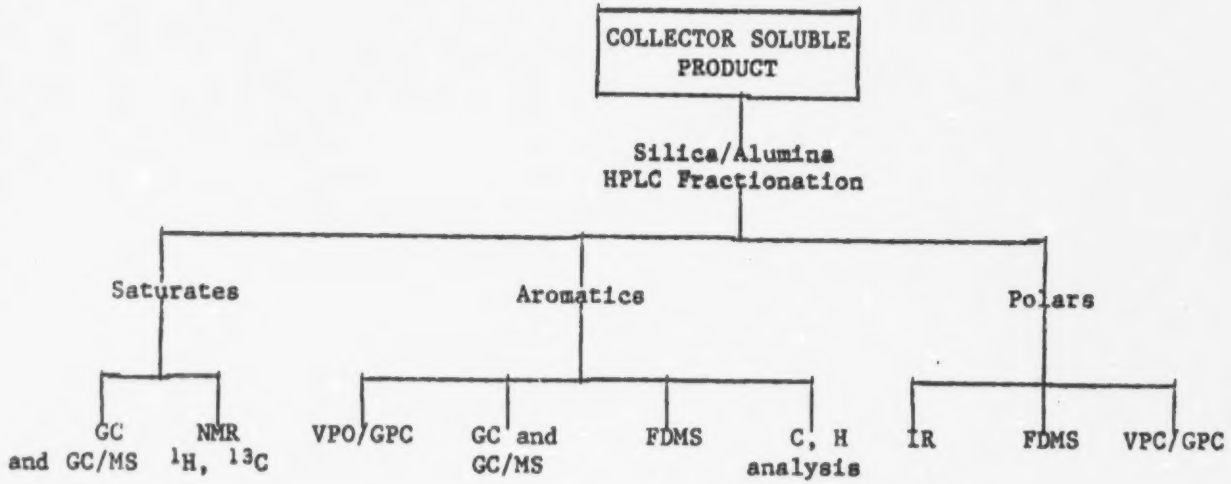
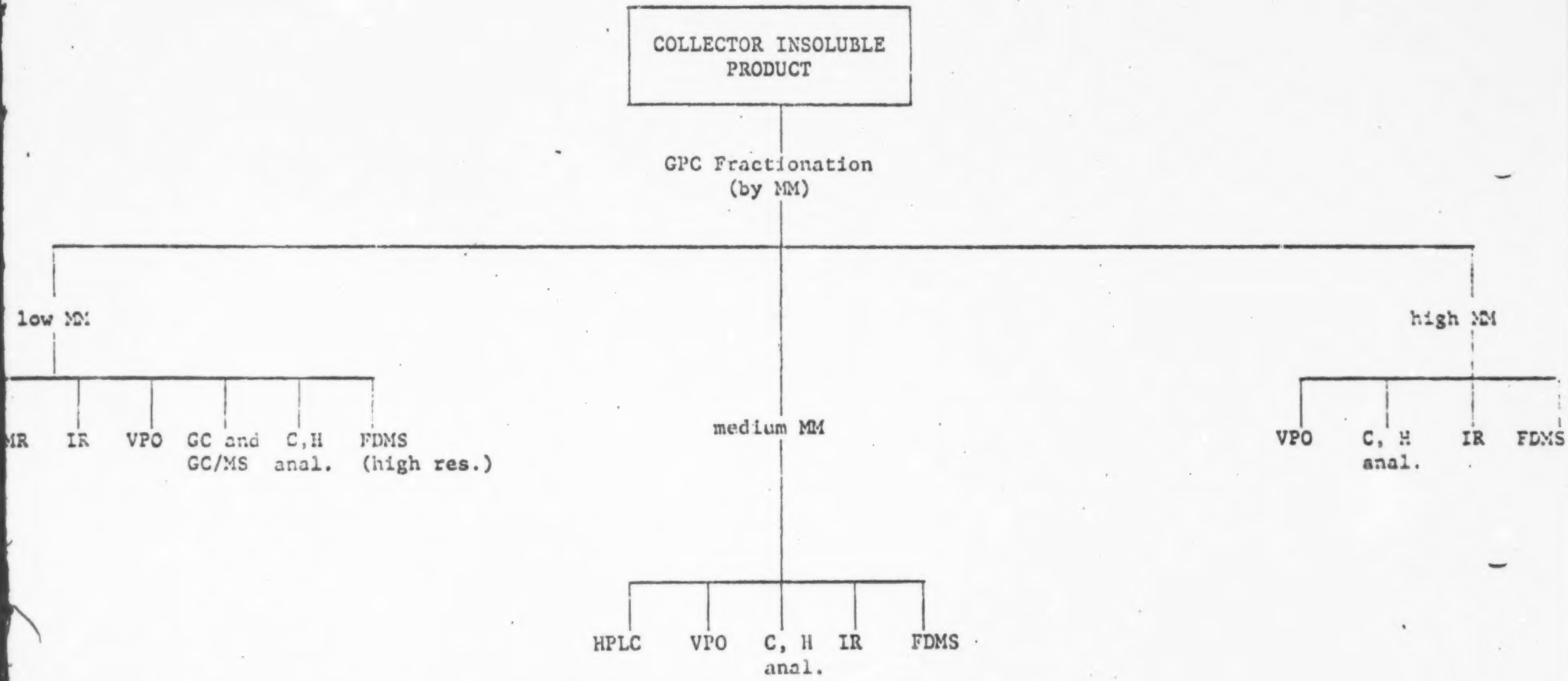


Figure 3. ANALYTICAL SCHEME FOR COLLECTOR INSOLUBLE PRODUCT



APPENDIX II.3.2

SAMPLE PREPARATION FOR IR ANALYSIS

SAMPLE PREPARATION FOR IR ANALYSIS

The $CDCl_3$ solutions used for proton NMR were adjusted in concentration by the addition or evaporation of $CDCl_3$ and the solution was put into a liquid film IR cell (NaCl plates). $CDCl_3$ was placed in the matching reference cell.

APPENDIX II.3.3

INFRA-RED ANALYSIS PROCEDURE

INFRA-RED ANALYSIS

IR spectra were recorded of samples as solutions in chloroform-d using a Perkin-Elmer Model 283 dual-beam spectrophotometer. The "normal" settings were used to record spectra using balanced cells.

APPENDIX II.3.4

SEP-PAK FRACTIONATION OF COAL LIQUIDS

SEP-PAK FRACTIONATION OF COAL LIQUIDS

Sep-Pak cartridges are mini-chromatography columns. Waters Associates Sep-Pak (Part No. 51900) silica cartridges were used to fractionate the toluene or chloroform soluble fractions of the coal liquids. The sample could be fractionated by washing through the Sep-Pak with solvents of varying polarity. A mixture of dichloromethane and pentane in the ratio of 25/75 was found to preserve all of the GC volatile material in the sample while at the same time leaving the maximum amount of non GC-volatile material on the Sep-Pak.

The Sep-Pak was left in its sealed foil envelope until just before use. The sample, which had been stored in $CDCl_3$ was poured into a pre-weighed 100 ml round bottom flask. The vial was rinsed with CH_2Cl_2 and poured into the flask. The sample was taken to dryness on a rotary evaporator and the flask re-weighed to determine the weight of the sample.

The sample was redissolved in approximately 2 ml of CH_2Cl_2/C_5H_{12}. A pre-weighed 50 ml round bottom flask with a B24 neck was placed in a 250 ml beaker. The Sep-Pak was removed from its envelope and the long end attached to the luer lock of a 5 ml syringe. The Sep-Pak-syringe was held inside the 50 ml flask with the plunger removed. A clean Pasteur pipette with 1 ml bulb was used to transfer the sample into the syringe barrel. The sample flask was rinsed with CH_2Cl_2/C_5H_{12} and the rinse solution added to the syringe. The plunger was inserted into the syringe and the sample pushed through the Sep-Pak. The syringe barrel was filled with the CH_2Cl_2/C_5H_{12} mixture and flushed through again. This was repeated until approximately 15 mls of solvent had been used or until the effluent from the Sep-Pak was very lightly coloured. The sample was taken to dryness on a rotary evaporator and weighed.

APPENDIX II.3.5

SAMPLE PREPARATION FOR GAS CHROMATOGRAPHY

SAMPLE PREPARATION FOR GAS CHROMATOGRAPHY

The concentration desired for GC and GC/MS analysis was approximately 0.0150 g of dry sample per 2 ml of CH_2Cl_2; this gave a full-scale signal when 1 µl was injected at an attenuation of 32×10^{-12} on the Varian 2440 GC. The concentration of the sample after fractionation on the Sep-Pak (see Appendix II.3.4), was adjusted to this range by adding the appropriate amount of CH_2Cl_2. The sample was ready for GC analysis and transferred to a Pierce 3.5 ml screw cap septum vial with 12 mm Pierce TufBond Teflon/Silicone disc.

APPENDIX II.3.6

GAS CHROMATOGRAPHIC ANALYSIS PROCEDURE

GAS CHROMATOGRAPHIC ANALYSIS PROCEDURE

Gas chromatograms were recorded using a Varian 2440 gas chromatograph equipped with a flame ionization detector; a Hewlett-Packard 3390A Reporting Integrator was used in conjunction with the gas chromatograph (GC). The GC has been modified for use with capillary columns and to allow the sample to be injected directly onto the column, to avoid possible pyrolysis in a heated injection block.

Analyses were conducted using a 30m x 0.22m(ID) WCOT fused silica capillary column with SE-54 liquid phase (Chromatographic Specialties). Helium was used as the carrier gas with a linear flow velocity of 60 cm/sec. Generally the sample concentrations were adjusted to bring the signal on scale with the attenuation set at 32×10^{-12}, such concentrations being appropriate for GC/MS analysis.

1 ul samples were injected directly on to the column with the column at 30^{o}C. This temperature was held for 3 minutes and the temperature increased at 6^{o}/minute to 290^{o} where the temperature was held for approximately 20 minutes.

APPENDIX II.3.7

SAMPLE PREPARATION

FOR

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

SAMPLE PREPARATION FOR GC/MS ANALYSIS

The sample was fractionated as described in Appendix II.3.4 and the concentration adjusted so that 1 µl at attenuation of 32×10^{-12} gave a full scale signal on the Varian 2440 GC. This concentration was suitable for GC/MS analysis.

For the GC/MS analysis an internal standard was added to the solution. The internal standard contained:

naphthalene;	signal appeared at 20.0 minutes*
Phenanthrene;	signal appeared at 30.7 minutes*
anthracene;	signal appeared at 30.9 minutes*
chrysene;	signal appeared at 41.2 minutes*

---

* Retention times on Varian 2440 GC with conditions as described in Appendix II.3.6.

APPENDIX II.3.8

GC/MASS SPECTROMETRIC ANALYSIS PROCEDURE

GC/MASS SPECTROMETRIC ANALYSIS PROCEDURE

GC/MS data were recorded on a Finnigan 3300 instrument. A 30m x 0.32mm ID, SE-54 fused silica capillary column (Chromatographic Specialties) was used as the GC column. Samples as solutions in chloroform or pentane were injected directly onto the column at room temperature. Three minutes after the solvent started to elute, the oven temperature was raised to 60^oC and the temperature increased at 6^oC per min. to 280^o whre it was held until no further peaks were observed. Chemical ionisation (CI) and electron impact ionisation (EI) spectra were recorded on separate trials. Mass spectra were stored in a PDP-11/23 based data system prior to printout and for data manipulation.

Identification of components: Preliminary identifications of individual components was accomplished by the search routine of the data system. The initial screen was based on the GC retention index and component molecular weight. The GC column was precalibrated using naphthalene, phenanthrene and chrysene as retention index standards. These were then added as internal standards in the samples. The identification program calculates the retention index of the peak relative to the internal standards. This retention index is then compared, together with the molecular weight (also determined from the CI spectrum by the program), with a library within the data stystem and a preliminary identification given. The retention index window is ±1% and has proven to be consistent through changes in the column (provided the same active phase is used) over a 1 year period using the algorithms we have developed. Further identification of the components is provided by comparison of the EI spectrum with the EPA/NIH mass spectral reference library.

APPENDIX II.3.9

SAMPLE PREPARATION FOR NMR ANALYSIS

SAMPLE PREPARATION FOR NMR ANALYSIS

After complete removal of the solvent from toluene or chloroform solubles (Appendix II.1.7), samples were dissolved in chloroform-d ($CDCl_3$), placed in vials and stored in a freezer. Concentrations were adjusted by evaporation of $CDCL_3$ and transferred to NMR tubes.

The pyridine soluble fractions were dissolved in pyridine-d_5 for NMR spectra. However incomplete removal of pyridine prior to dissolution in pyridine-d_5 has, to date, prevented the acquisition of satisfactory NMR spectra of this fraction. Procedures used for pyridine removal are described in Appendix II.1.9.

APPENDIX II.3.10

NMR ANALYSIS PROCEDURE

NMR ANALYSIS PROCEDURE

^{1}H-NMR spectra were routinely recorded either at 90 MHz or 60 MHz using Perkin-Elmer R32 or R12B NMR spectrometer respectively. Selected NMR spectra were recorded using a Brücker WP250 Fourier Transform instrument.

Integration of NMR signals was carried out three times for each sample; the values for the aromatic region (5.5-9.0 ppm) and the aliphatic region (0.5-4.5 ppm) were taken as the average of the integration trials. Corrections for the signal from the solvent ($CDCl_3$ contains traces of $CHCl_3$) were obtained by integration of the NMR signal of the solvent.

NMR spectra of some toluene and pyridine soluble fractions derived from the initial sample work-up procedure (Appendix II.1.2b) showed the presence of tetrapropylammonium iodide. This salt was removed by washing with water (one or two washes were normally adequate). The wash of the pyridine solubles was dark and viscous indicating that other material was being removed. After the adoption of the improved work-up procedure (Appendix II.1.2) the NMR spectra of the solutions gave no indication of tetrapropylammonium iodide.

APPENDIX II.3.11

PREPARATION OF SAMPLES
FOR
MOLECULAR WEIGHT DETERMINATION

PREPARATION OF SAMPLES FOR MOLECULAR WEIGHT DETERMINATION

Chloroform-d was evaporated from the sample with a stream of nitrogen. The 6 dram storage vial filled with approximately 15 ml of spectral grade benzene and swirled to ensure complete dissolution of the sample. Approximately 4 ml of the benzene solution was taken into a 5 ml glass syringe to which a Millipore Swinny filtration apparatus (with fresh GSWP 013 00 filter) was attached. The solution was filtered into a clean, dry 50 ml round bottom flask. The filtration apparatus was removed from the syringe and the syringe refilled. The procedure was repeated until all of the solution had been filtered. The filter was then flushed once with clean benzene.

The benzene was removed from the filtrate on a rotary evaporator, the final traces of benzene being removed on a vacuum line (approximately 15 minutes).

Working in a fumehood, a Pasteur pipette was used to add 2 - 3 ml of spectral grade CS_2 to the dry residue and the sample was swirled to ensure dissolution. This solution was transferred, using another Pasteur pipette, into a labelled, clean, dry, pre-weighed (to 4 decimal places) 10 ml volumetric flash. (The volumetric flask should be handled with gloved hands until the final weighing). The 50 ml flask was rinsed with small volumes of CS_2 until the CS_2 was colourless. All volumes of the CS_2 were added to the volumetric flask.

The unstoppered volumetric flask was placed under a stream of nitrogen to evaporate the CS_2. This was best accomplished by the nitrogen being directed gently on to the surface of the solution through a clean, dry Pasteur pipette inserted just inside the volumetric flask. All the CS_2 was evaporated. If CS_2 could be detected, by smell, the sample required additional evaporation.

The flask was weighed to 4 decimal places on the analytical balance and the value recorded together with the original weight.

The solution was made up to the mark with spectral grade benzene and the flask stoppered.

APPENDIX III.3.12

DETERMINATION OF MOLECULAR WEIGHT BY VAPOUR PHASE OSMOMETRY

DETERMINATION OF MOLECULAR WEIGHT BY VAPOUR PHASE OSMOMETRY

Samples were prepared as described in Appendix II.3.11. Weight of the sample was recorded and the concentration, C, in grams per kilogram of benzene found. When working with the samples and solvents, gloves were worn and work performed in the fumehood.

Standards of known concentrations were made with benzil of concentrations from 1 to 6 millimole/kg. The benzil was weighed on an analytical balance to 4 decimal places and transferred to a labelled 100 ml volumetric flask. Spectral grade benzene was used to make the solution up to the mark.

A Hitachi Perkin-Elmer Model 115 Vapour Phase Osmometer was used and the instrument assembled for operation as described in the instrument manual. The operating temperatures were set at 36°C for the sub-oven and 41.5°C for the main oven for benzene. Approximately 10 ml of benzene was required to fill the thermistor block. This was added with a Pasteur pipette before assembly, allowing faster equilibration. Addition of solvent by the inject port is not recommended as the instrument does not equilibrate afterward.

Benzene and samples were added to the injection syringes of the instrument with Pasteur pipettes. One-third turns of the injection knobs were used to deliver solvents and samples from the injection syringes to the thermistors.

The instrument must be equilibrated before samples were run (*i.e.* a 1/3 turn of the S.V. sampling knob produced deflection of the meter to the left of 0 only; and a 1/3 turn of the R.V. sampling knob produced deflection to the right of 0 only). The needle must return to rest at 0.

Measurement of the change in resistance of the thermistors (ΔR) were performed as directed in the instrument manual. At least 3 benzil standards were made. If the values fitted the calibration curve, (see graph), then the unknown samples could be run. The slope may differ slightly, but it must go through zero. If the values of ΔR do not fall on this line, the standards are remade or the troubleshooting directions are followed in the instrument manual.

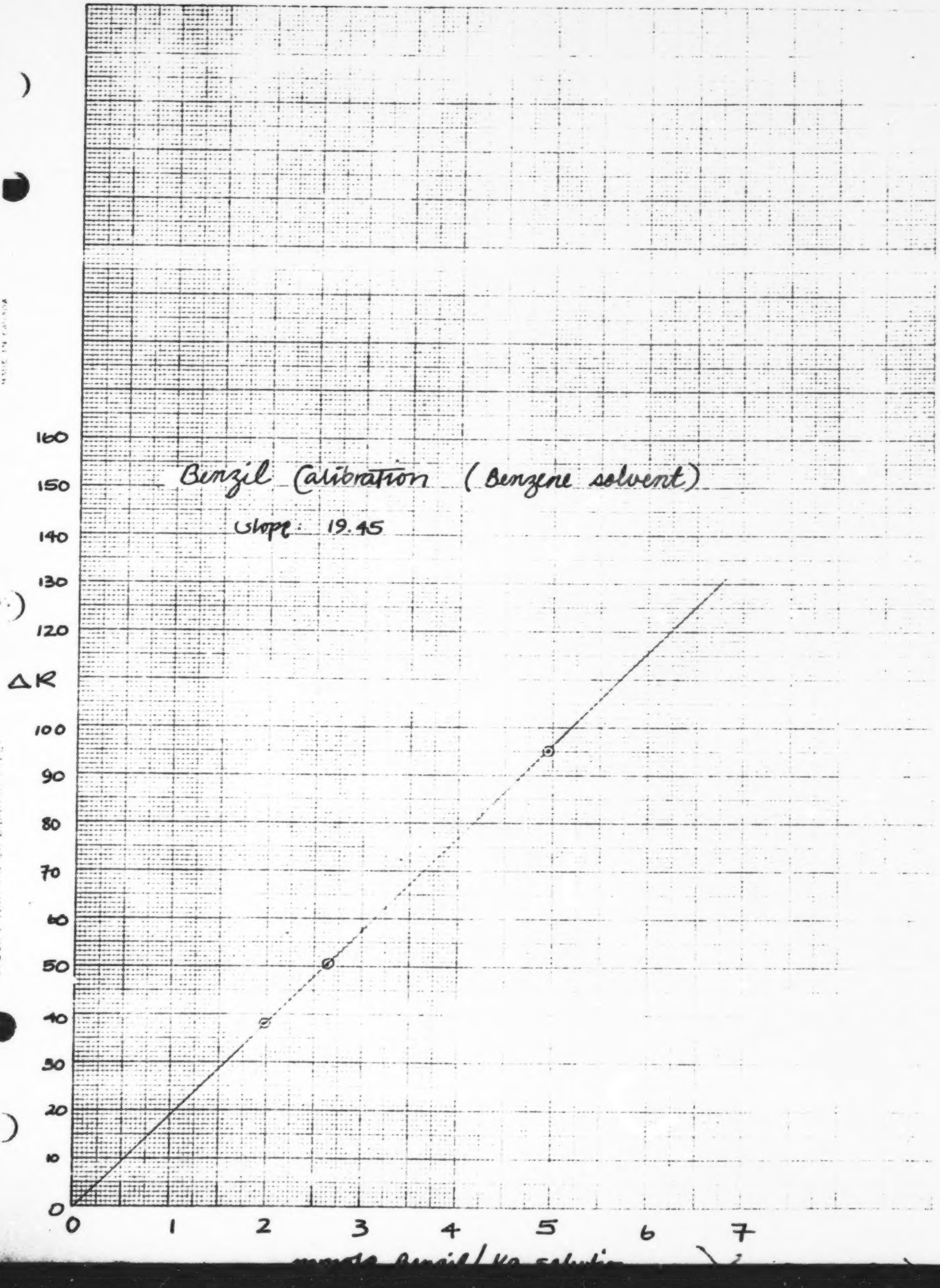
The instrument was best equilibrated, between 3 hours and 3 days after being turned on. If equilibration could not be reached, the thermistor block was disassembled, dried out, 10 ml of benzene added, the block reassembled and turned on.

Calculations for $\Delta R/C$ and Mn were completed as in the instruction manual, *i.e.*

K (instrument constant) = slope of calibration graph x 1,000

Mn (molecular weight) = $\frac{K}{\Delta R/C}$ for each sample

K for graph given = 19,450 , therfore Mn = $\frac{19{,}450}{\Delta R/C}$



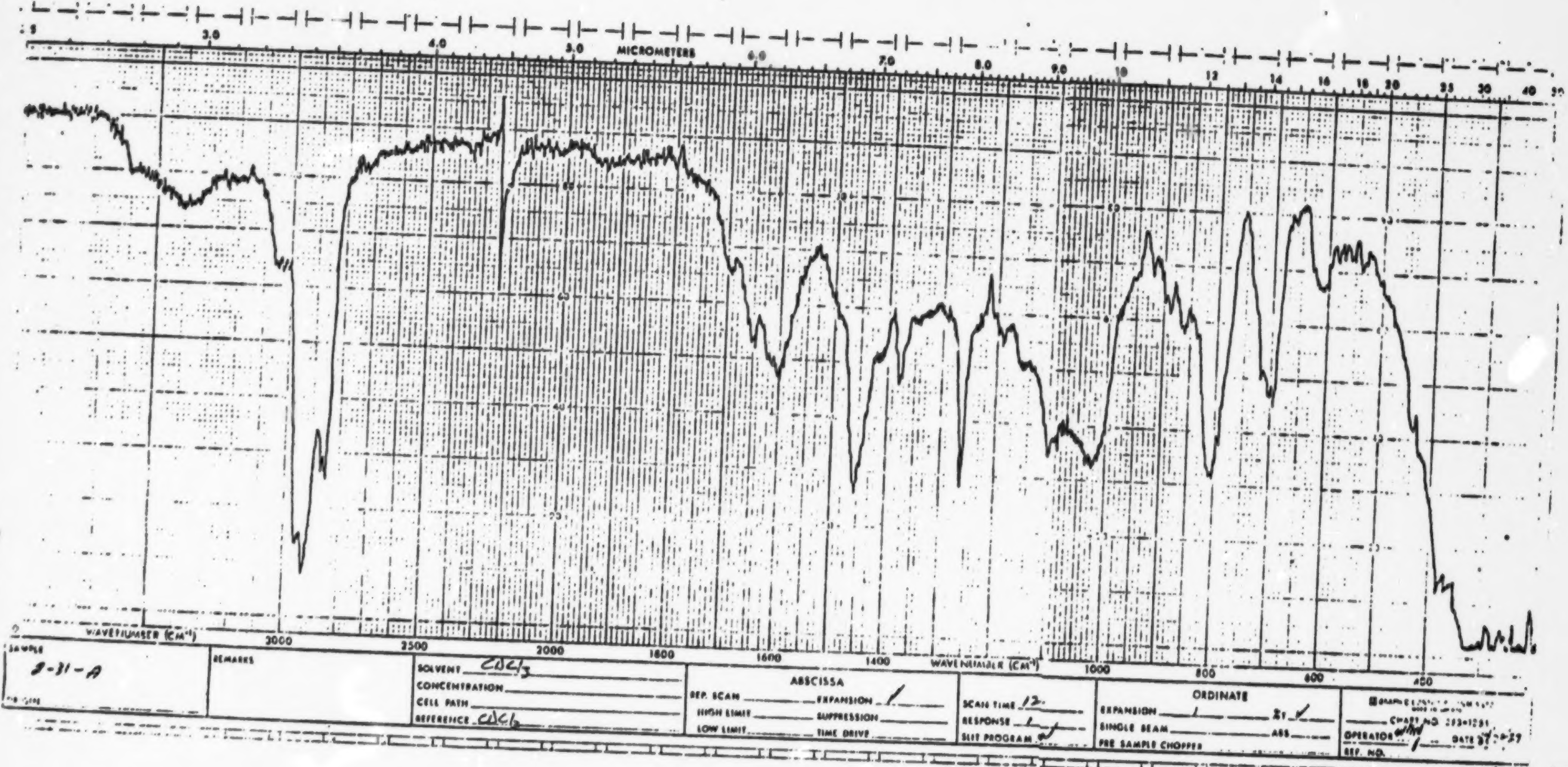
Benzil Calibration (Benzene solvent)

Slope: 19.45

APPENDIX II.3.13

INFRA-RED SPECTRA

Figure 1. Sample 2-31-A. Toluene extract of K-seam coal/clathrate experiment.



SAMPLE 2-31-A

REMARKS

SOLVENT CDCl3
CONCENTRATION
CELL PATH
REFERENCE CDCl3

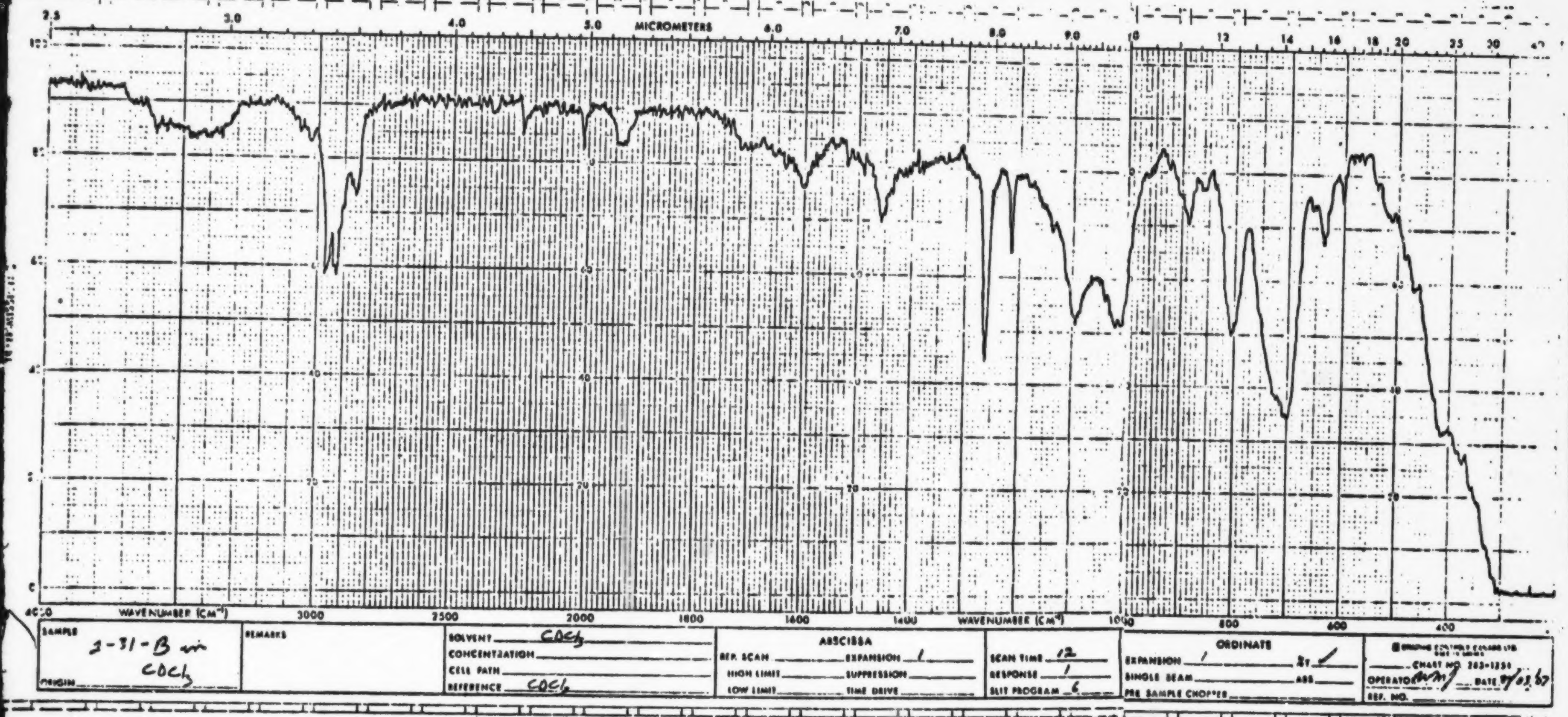
REP. SCAN
HIGH LIMIT
LOW LIMIT
EXPANSION 1
SUPPRESSION
TIME DRIVE

SCAN TIME 12
RESPONSE 1
SLIT PROGRAM

EXPANSION 1
SINGLE BEAM
PRE SAMPLE CHOPPER
%T ✓
ABS

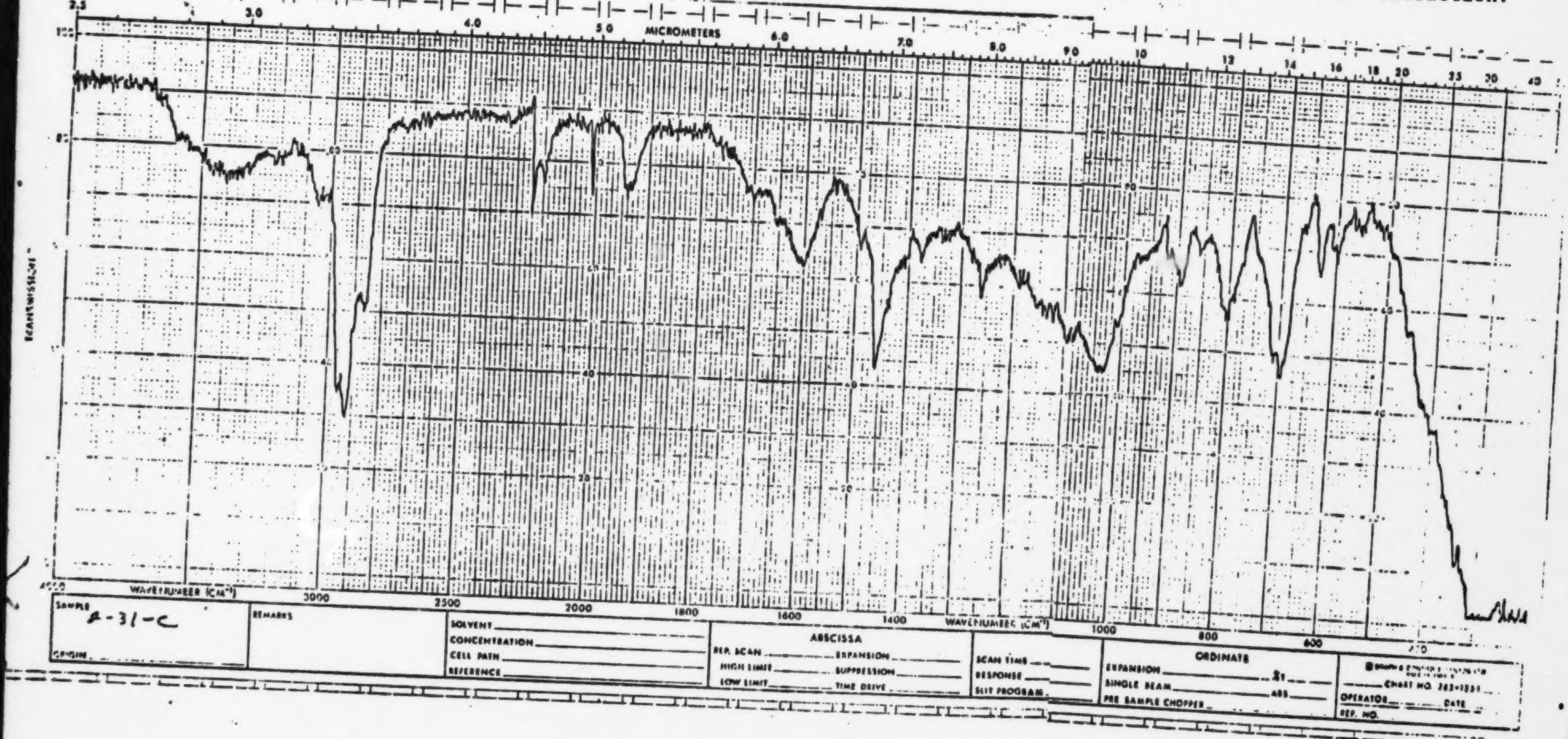
CHART NO. 273-1291
OPERATOR
DATE
REF. NO.

Figure 2. Sample 2-31-B. Chloroform extract of coal residue from K-seam coal/clathrate extraction.



SAMPLE 2-31-B in CDCl3
ORIGIN
REMARKS
SOLVENT CDCl3
CONCENTRATION
CELL PATH
REFERENCE CDCl3
ABSCISSA
REP. SCAN
HIGH LIMIT
LOW LIMIT
EXPANSION 1
SUPPRESSION
TIME DRIVE
SCAN TIME 12
RESPONSE 1
SLIT PROGRAM 6
ORDINATE
EXPANSION 1
SINGLE BEAM
PRE SAMPLE CHOPPER
%T 1
ABS
CHART NO. 263-1251
OPERATOR
DATE 9/03/67
REF. NO.

Figure 3. Sample 2-31-C. Chloroform extract of clathrate residue from K-seam coal/clathrate extraction.



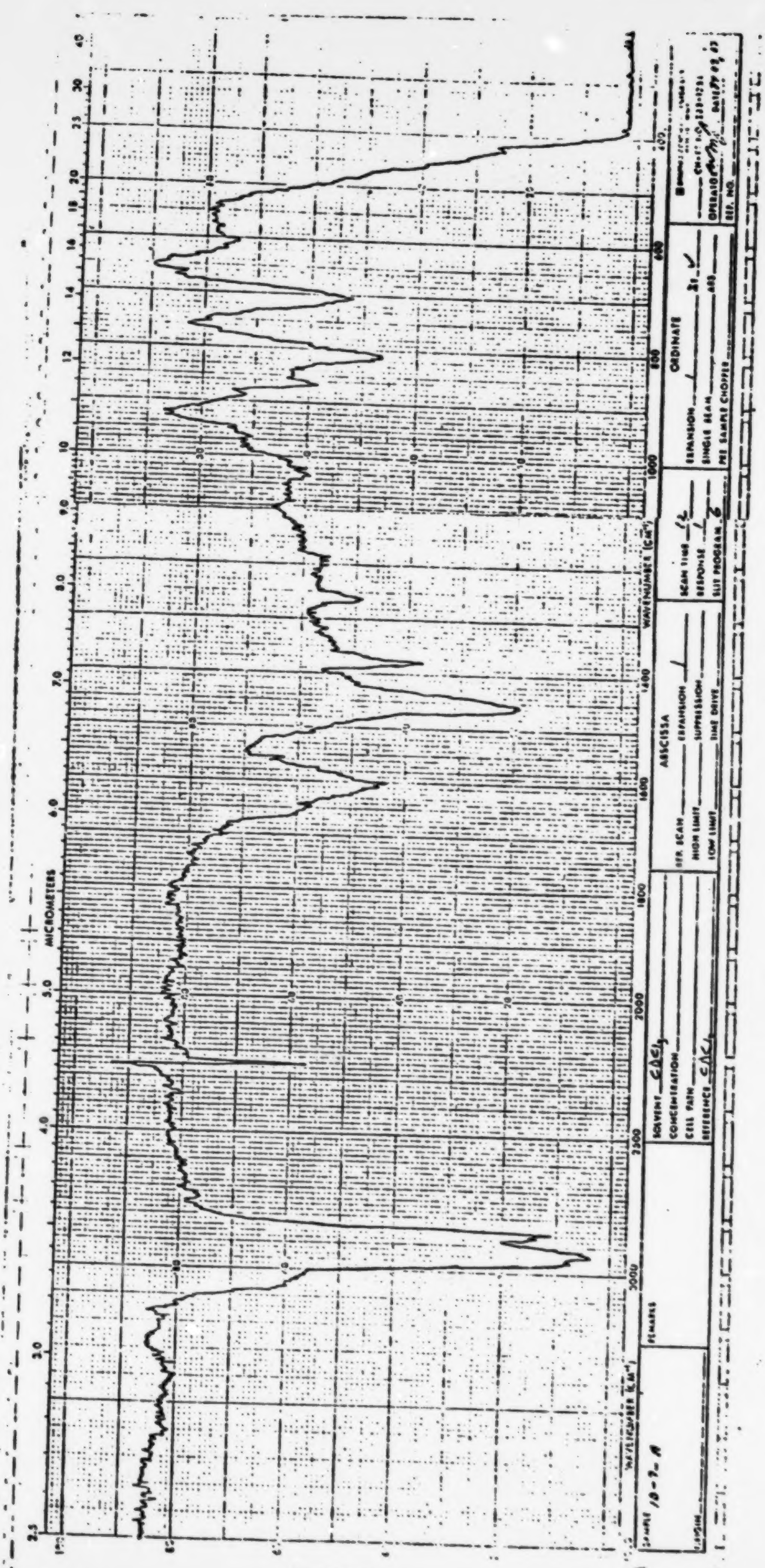


Figure 4. Sample 10-7-A. Toluene extract of Devco/clathrate experiment.

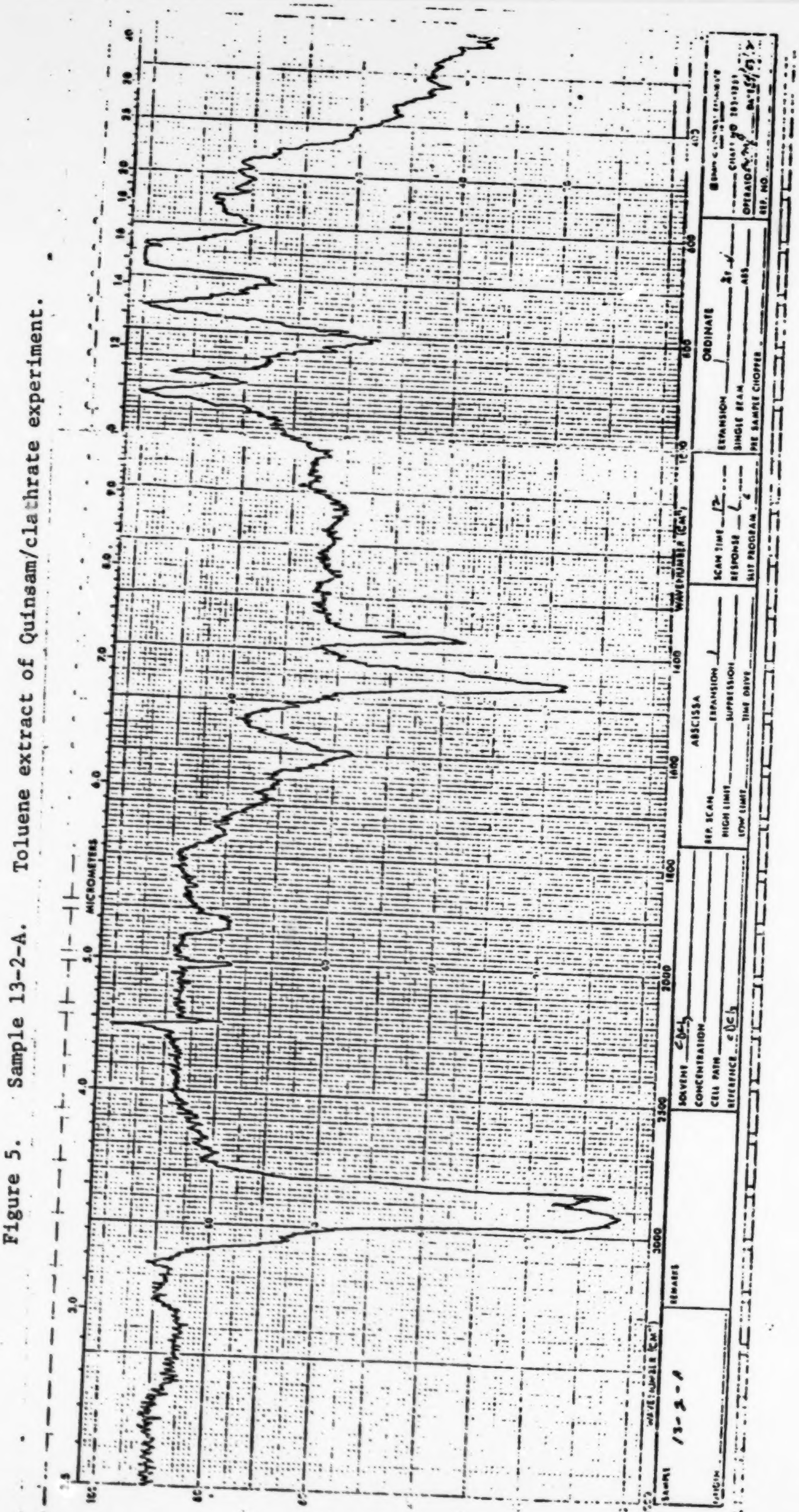


Figure 5. Sample 13-2-A. Toluene extract of Quinsam/clathrate experiment.

APPENDIX II.3.14

^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA

Figure 1. Sample 2-9A

Toluene soluble fraction of
Kcoal/clathrate extraction.

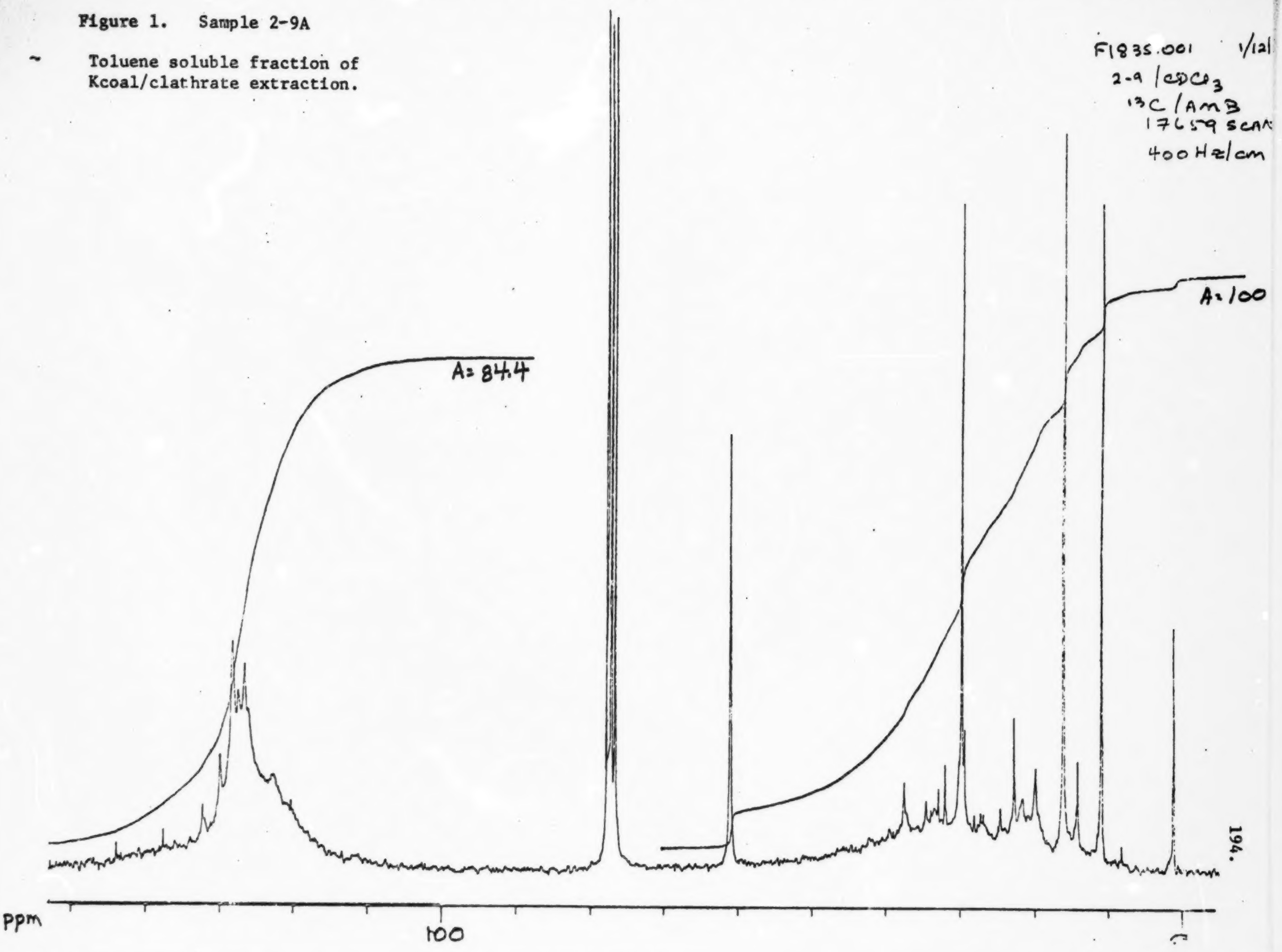
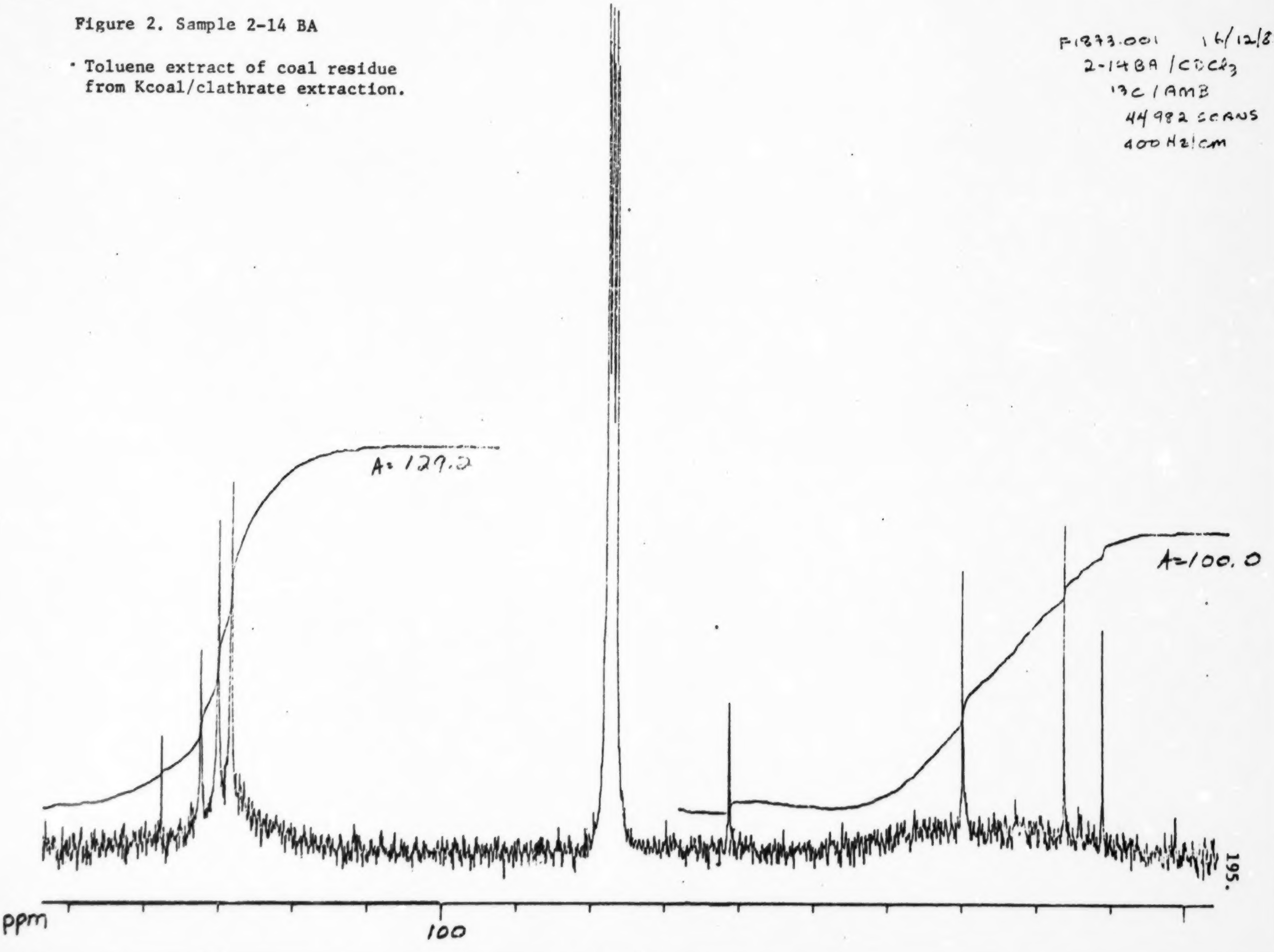


Figure 2. Sample 2-14 BA

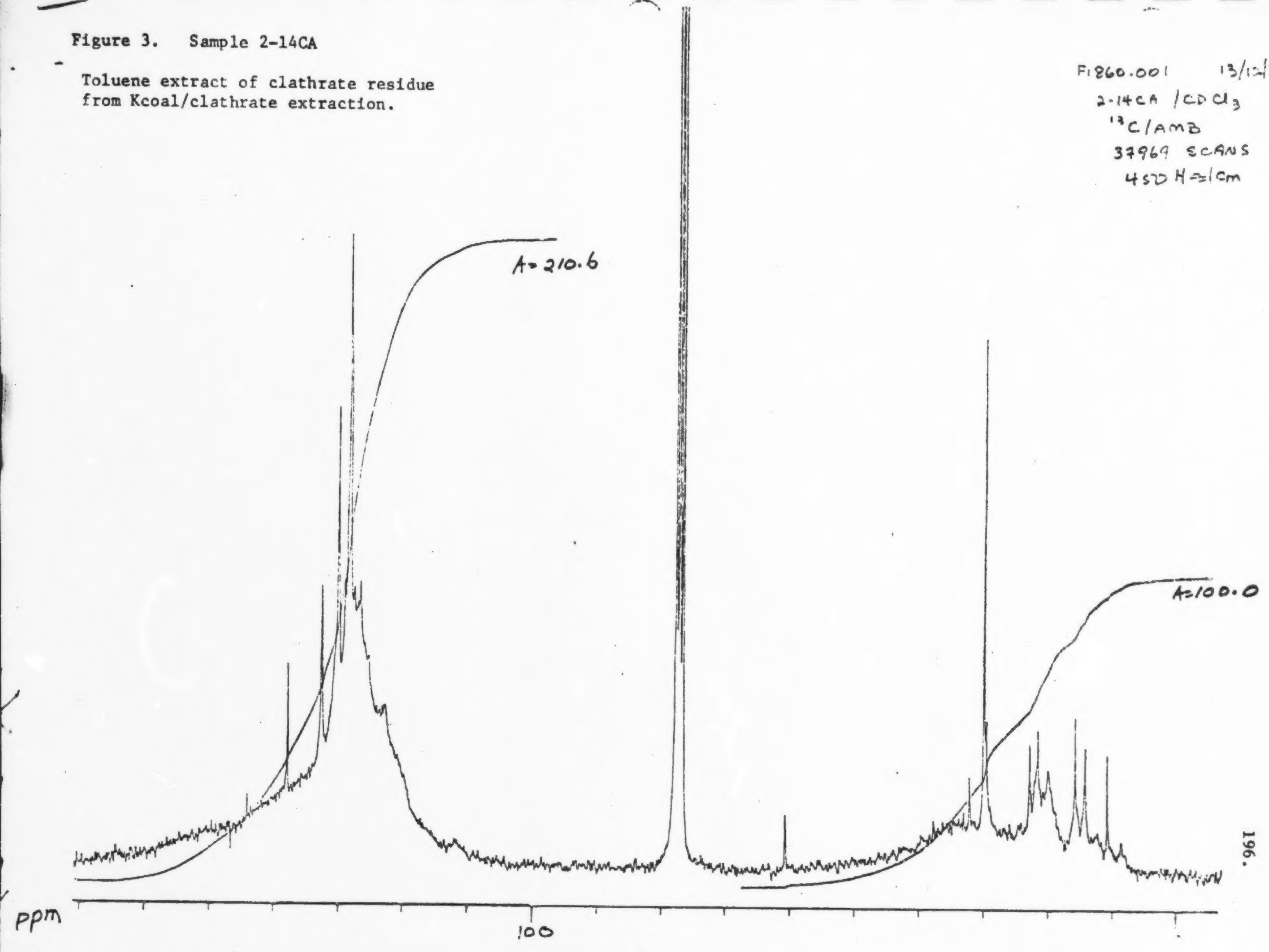
· Toluene extract of coal residue from Kcoal/clathrate extraction.



F1873.001 16/12/83
2-14BA /CDCl3
13C /AMB
44982 SCANS
400 Hz/cm

Figure 3. Sample 2-14CA

Toluene extract of clathrate residue from Kcoal/clathrate extraction.



F1860.001 13/12/8

2-14CA /$CDCl_3$

^{13}C/AMB

37969 SCANS

4SD H≈1cm

APPENDIX II.3.15

GAS CHROMATOGRAMS

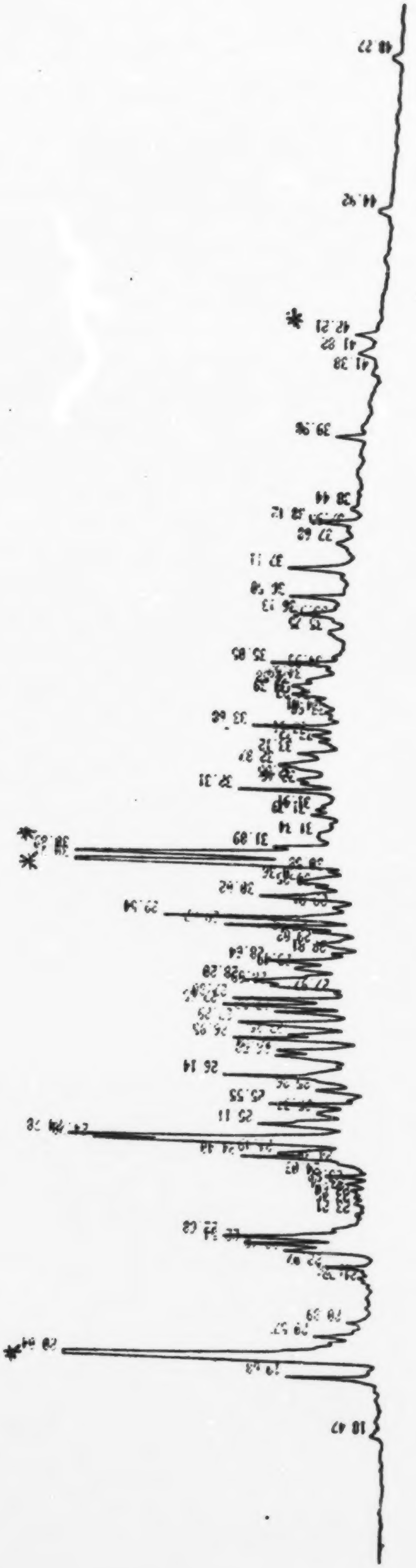
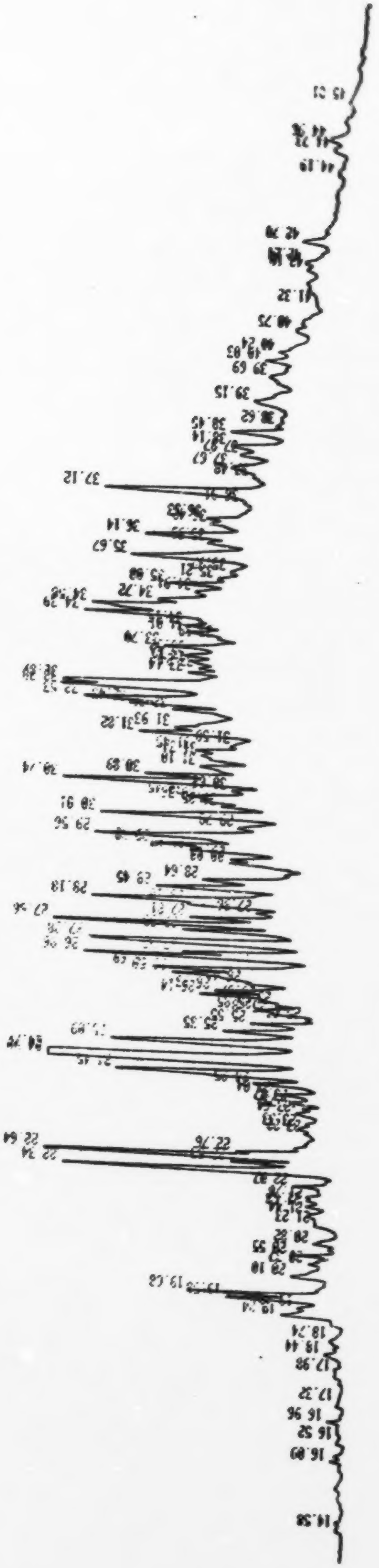


Figure 1. Sample 2-21-4

Toluene Soluble Fraction
*napthalene, phenanthrene, anthracene and chrysene added as internal standards.

Figure 2. Sample 2-21-4

Chloroform extract of coal residue.



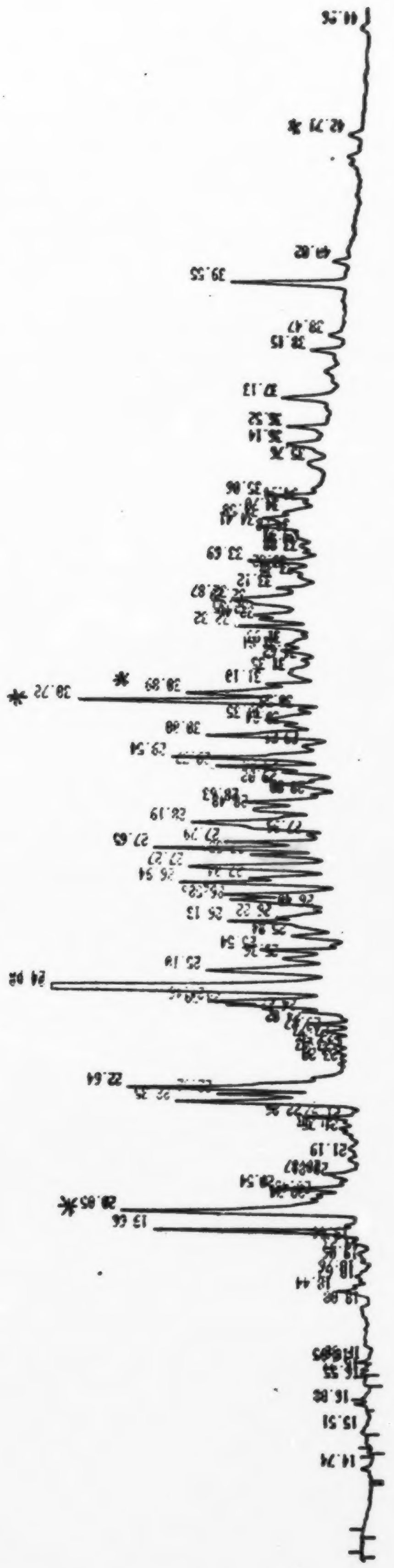
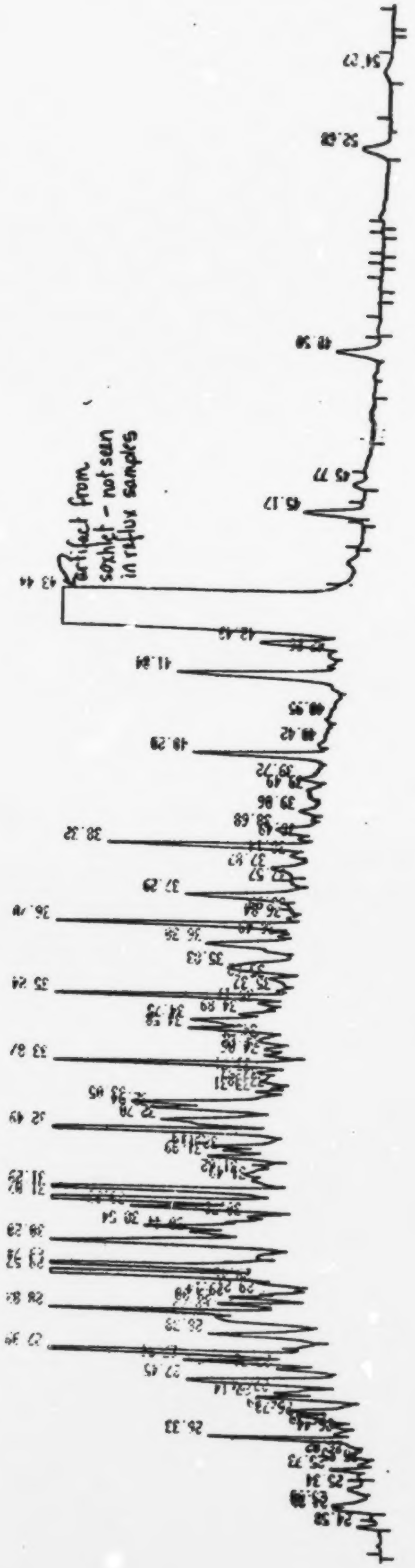


Figure 3. Sample 2-21-4

Chloroform extract of clathrate residue.

Figure 4.

Toluene soxhlet extraction of K-seam coal.



APPENDIX II.4.1

PREPARATION
OF
TRANSITION METAL SUSTAINED LIQUID CLATHRATES

PREPARATION OF TRANSITION METAL SUSTAINED LIQUID CLATHRATES

Preparations of all liquid clathrates were conducted in an inert atmosphere glove box. The procedure described is for a specific example, but was essentially the same for both the iron and manganese containing liquid clathrates.

2.30 g (5.53 m mole) of $[(\text{tetralin})\,\text{Mn(CO)}_3)]\text{PF}_6$ was placed inside a schenk tube and transferred to the inert atmosphere glove box. 100 ml of toluene was poured over the light yellow solid, with no discoloration of the toluene being observed. 1.5 ml (11.06 m mole) of AlEt_3 was added dropwise and almost immediately a light yellow clathrate layer began to form. Further AlEt_3 was added dropwise (3 ml, 22.12 m mole) until all the solid dissolved, giving ~30 ml of yellow (orange) liquid clathrate beneath the toluene phase. Tentatively, the liquid clathrate is formulated as having the formula $[(\text{tetralin})\text{Mn(CO)}_3][\text{Al}_6\text{Et}_{18}\text{PF}_6]$ (1), however it is possible that AlEt_3 molecules could attach themselves to the carbonyl moieties of the cation.

---

(1) Atwood has shown that more than 2 molecules of AlR_3 may complex to form liquid clathrate sustaining anions e.g. $(\text{Al}_4\text{Me}_{12}\,\text{SO}_4)^{2-}$: Rogers, R.D.; Atwood, J.L. Organometallics, 3, 263(1984).

APPENDIX II.4.2

^{1}H NMR (90MHZ) SPECTRA OF $[(arene)\ Fe(C_5H_5)]PF_6$ AND $[(arene)\ Mn(CO)_3]PF_6$ SALTS AND THEIR LIQUID CLATHRATES DERIVED FROM COMBINATION WITH $AlEt_3$ AND TOLUENE

^{1}H NMR (90MHZ) SPECTRA OF $[(\text{arene})\ Fe(C_5H_5)]PF_6$ AND $[(\text{arene})\ Mn(CO)_3]PF_6$ SALTS AND THEIR LIQUID CLATHRATES DERIVED FROM COMBINATION WITH $AlEt_3$ AND TOLUENE

Figure	Compound
1	(tetralin)$Mn(CO)_3\ PF_6$
2	(tetralin)$Mn(CO)_3\ PF_6/AlEt_3/$ toluene liquid clathrate.
3	(mesitylene)$Mn(CO)_3\ PF_6$
4	(mesitylene)$Mn(CO)_3\ PF_6/AlEt_3/$toluene liquid clathrate.
5	(tetralin)$Fe(C_5H_5)\ PF_6/AlEt_3/$toluene liquid clathrate.

Figure 1.

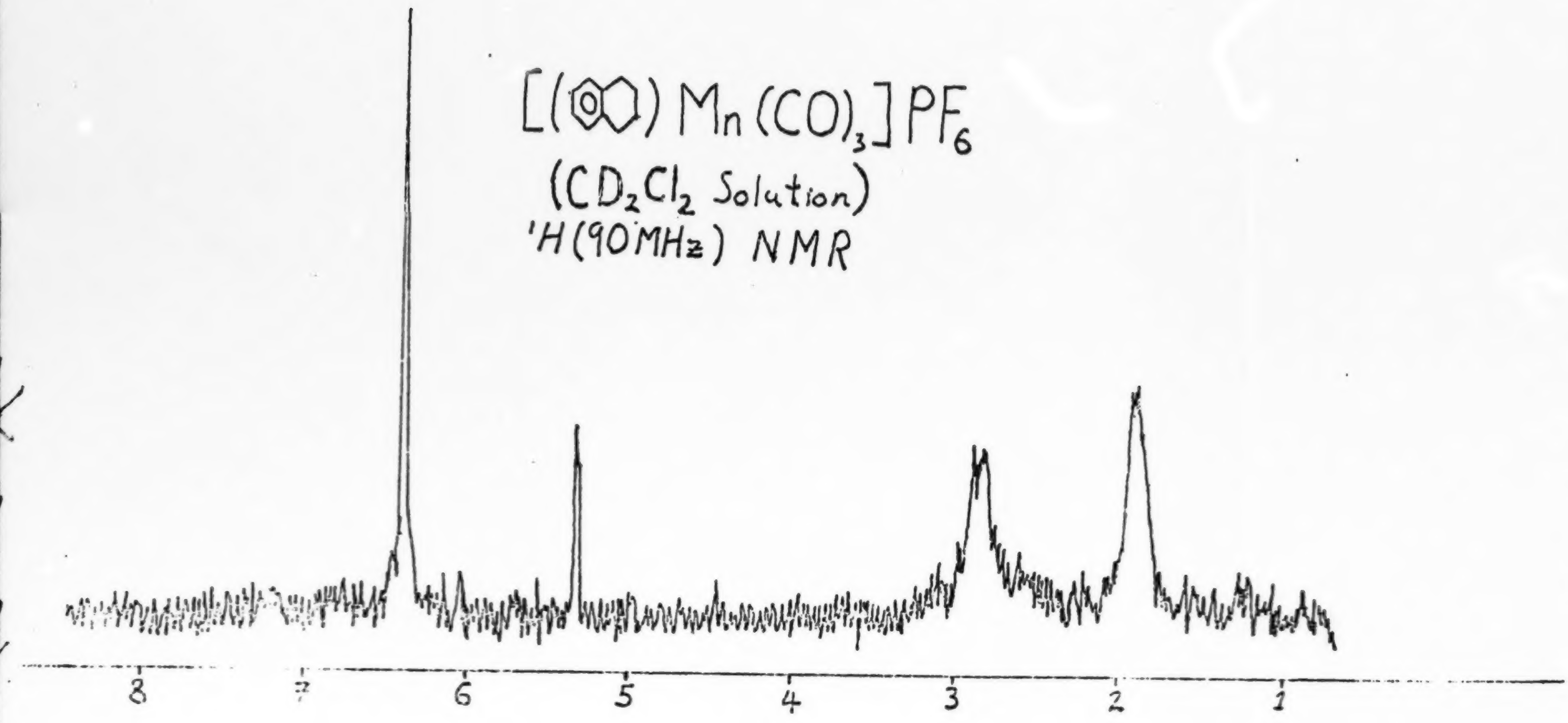


Figure 2.

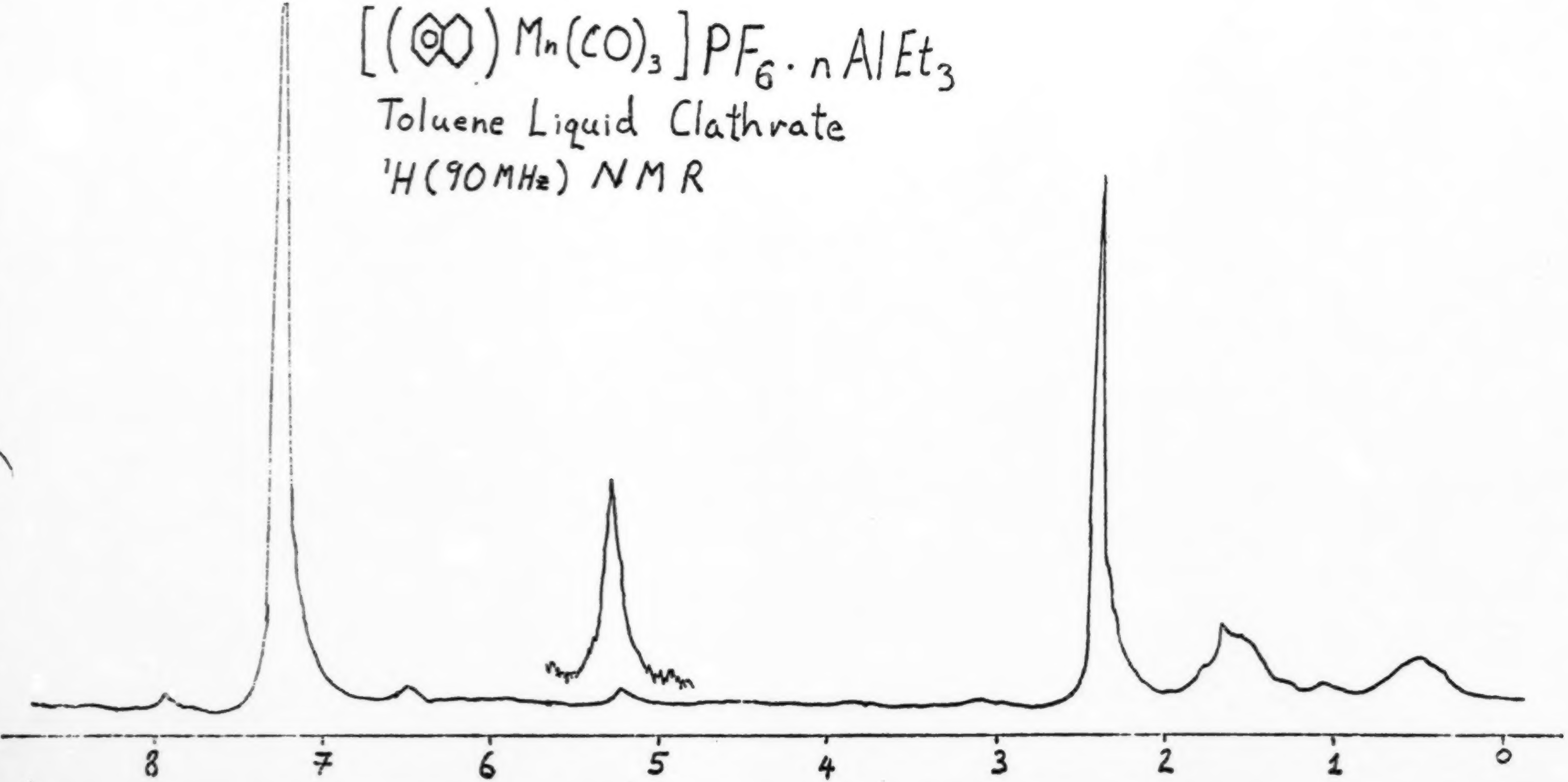

[( ) Mn(CO)₃]PF₆ · n AlEt₃
Toluene Liquid Clathrate
¹H (90 MHz) NMR
8
7
6
5
4
3
2
1
0

Figure 3.

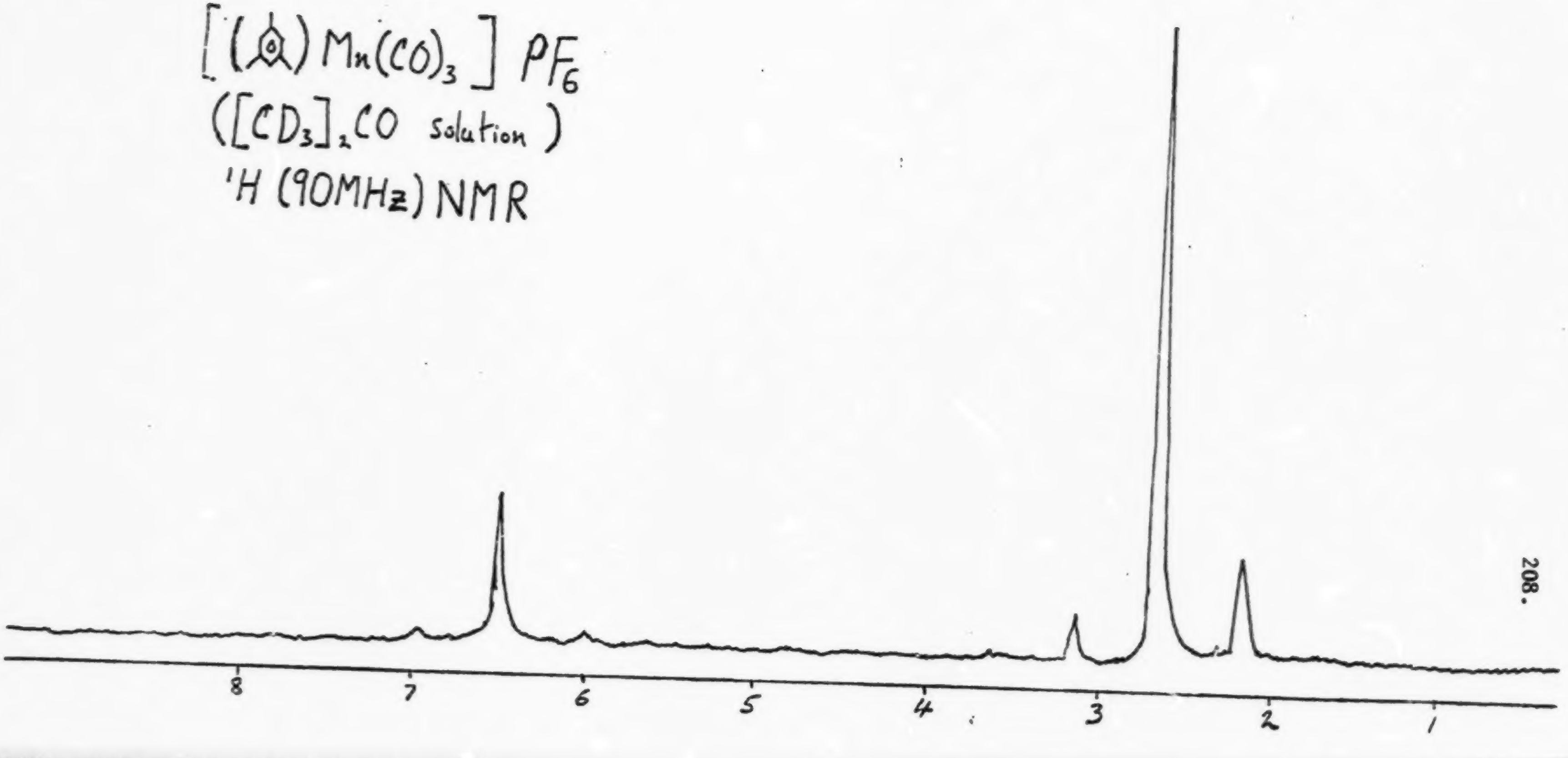


Figure 4.

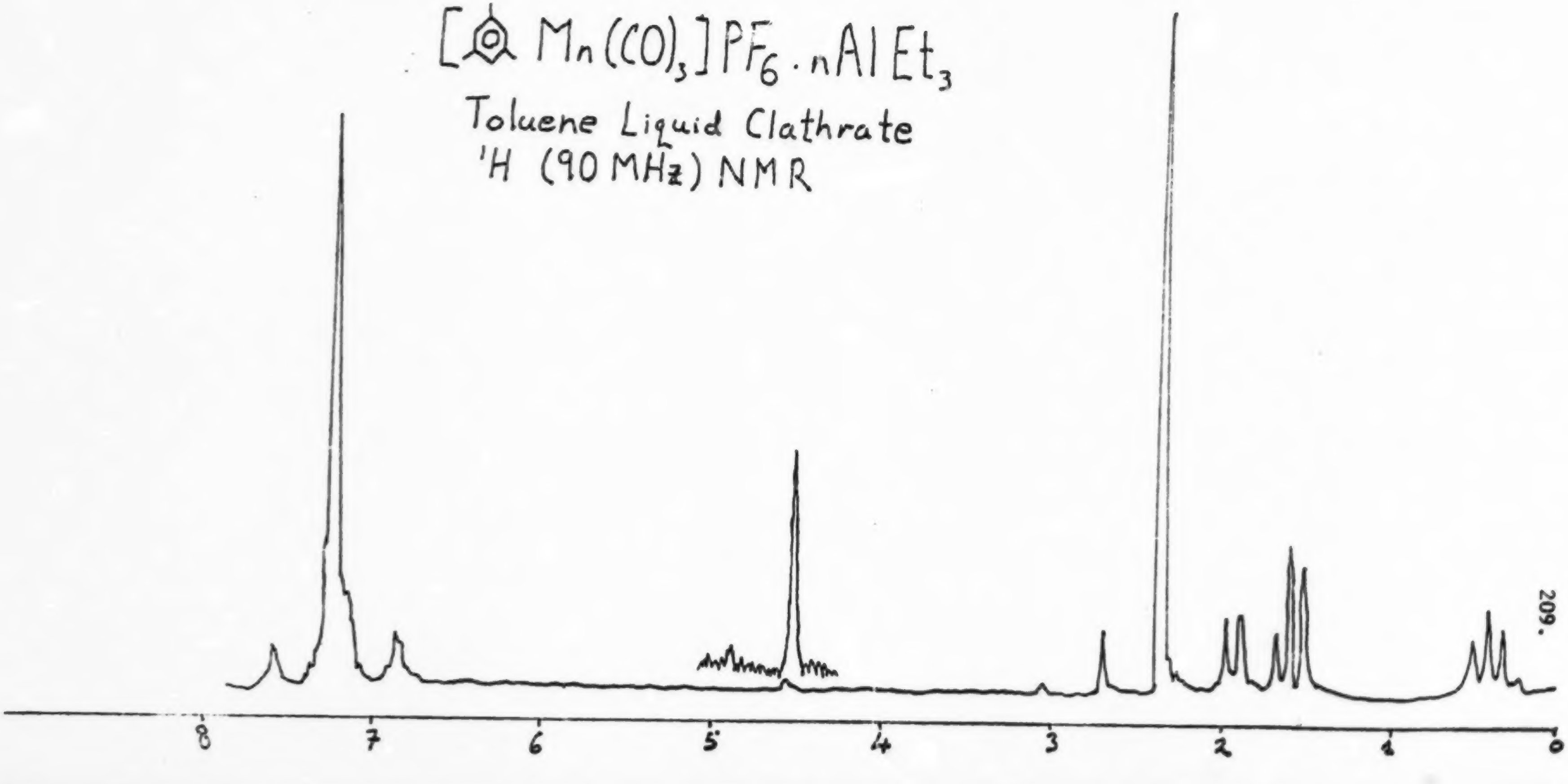
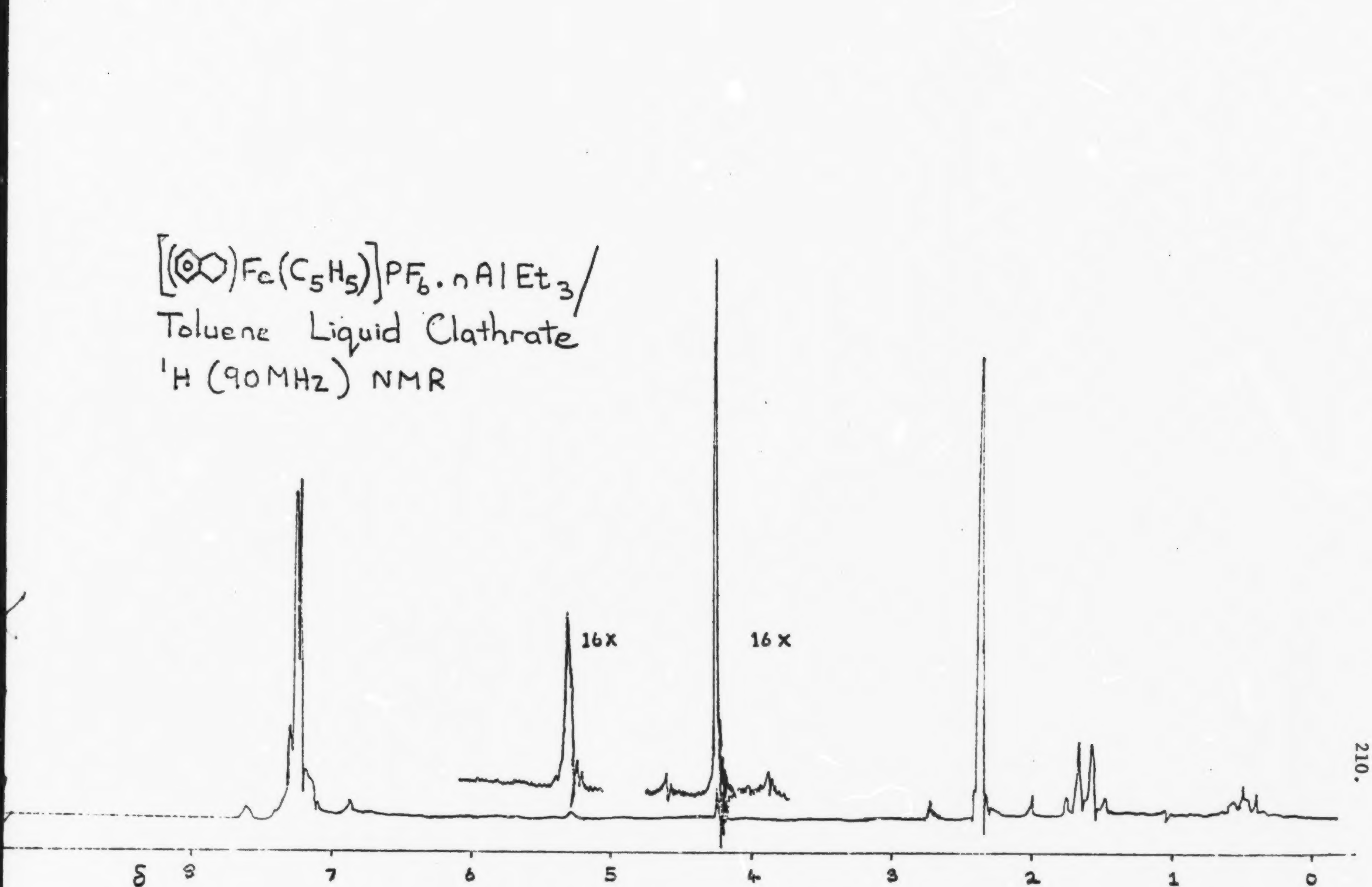

$[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn(CO)}_3]\text{PF}_6 \cdot n\text{AlEt}_3$
Toluene Liquid Clathrate
^{1}H (90 MHz) NMR
8
7
6
5
4
3
2
1
0

Figure 5.


[( )Fe(C$_5$H$_5$)]PF$_6$·nAlEt$_3$/
Toluene Liquid Clathrate
^{1}H (90MHz) NMR
16X
16X
δ 8
7
6
5
4
3
2
1
0

APPENDIX A

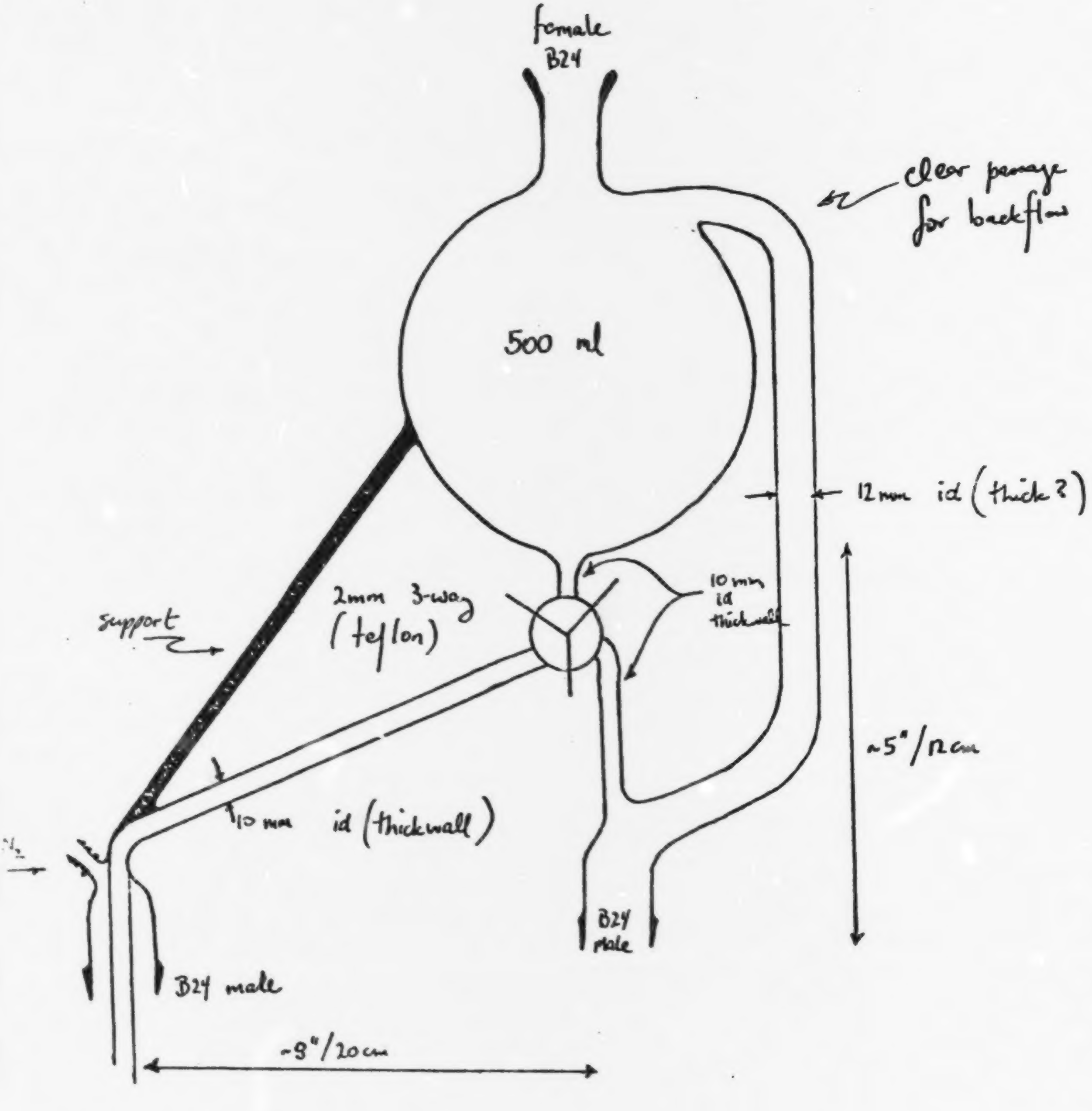
PURIFYING AND DRYING OF SOLVENTS

PURIFYING AND DRYING OF SOLVENTS

Approximately 4 g of sodium metal, wiped free of mineral oil and cut into small pieces, was added to 500 ml of toluene in a 1 litre flask. Approximately 3 g of benzophenone was added to act as an indicator when the toluene was dry. Another 500 ml of wet toluene was added to the flask and the flask set into a 1000 ml, 500 watt Thermowell heating mantle connected to an Armaco 1.4 KVA voltage regulator set at 80. A reflux/collecting apparatus with a 500 ml collecting bulb was set up. After filling the still and before turning it,on the system was flushed with nitrogen for about 2 minutes after which the flow was decreased and the reflux begun. After refluxing for approximately 1 hour 30 minutes, the indicator turned blue signifying that the toluene was dry and ready for distillation.

If the toluene still was used every day, after about one month sodium oxides formed in the bottom of the 1 litre flask and the colour of the indicator was always brown. White particles and a dark brown-black-colour when boiling indicated that the still needed cleaning.

The pyridine was dried and purified by reflux and distillation after adding about 3 g of sodium hydroxide to the wet pyridine. The still was set up in a fumehood and the voltage regulator set at 90. There was no colour indicator in the flask but after refluxing for 1 hour and 30 minutes the pyridine was dry and ready to be distilled.


female
B24
clear passage
for backflow
500 ml
12 mm id (thick?)
10 mm
id
thickwall
2mm 3-way
(teflon)
support
~5"/12cm
10 mm id (thickwall)
N_2
B24
male
B24 male
~8"/20cm

15/6/82 Ken.

APPENDIX B

INERT ATMOSPHERE GLOVE BOX OPERATION

INERT ATMOSPHERE GLOVE BOX OPERATION

The pyrophoric nature of triethylaluminum requires that it be stored and manipulated under rigorously oxygen and water free conditions. All liquid clathrate manipulations were conducted in an inert atmosphere glove box (a Vacuum Atmospheres Corporation HE-93-B-I model glove box obtained on loan from B.C. Research). Prepurified grade nitrogen was further purified by continuously recycling through oxygen and water scrubbers. The oxygen scrubber was regenerated daily using 6% hyrdrogen in nitrogen.

All materials were introduced to the dry box through an antechamber. The antechamber was evacuated for 5 minutes, refilled with pure nitrogen, and then evacuated for a further 10 minutes before any materials were introduced to the glove box.

APPENDIX C

SOURCES OF CHEMICALS

SOURCES OF CHEMICALS

I. a) Solvents

Solvents	Source	Grade
Acetone-d_6	MSD	99.6% D
Benzene	Kodak	Spectral Grade
Carbon disulphide	B.D.H.	Omnisolv
Carbon tetrachloride	Kodak	Spectral Grade
Chloroform	Caledon	Reagent
Chloroform-d	Aldrich	Gold Label
Dichloromethane	Terochem	Technical
Dichloromethane-d_2	Aldrich	99.6% D
Hydrochloric Acid	Amachem	Reagent
Mesitylene	Aldrich	97%
Tetralin	Aldrich	95%
Toluene	B.D.H.	Reagent
Toluene-d_8	MSD	99% D
Water	U.Victoria	Distilled

b) Reagents and Catalysts

Reagents and Catalysts	Source
Aluminum Trichloride	Aldrich
Ammonium hexafluorophosphate	Aldrich
Bromine	Allied Chemical
Cyclopentadienyl manganese tricarbonyl	Strem
Ferrocene	Aldrich
Manganese carbonyl	Strem
Mesitylene chromium tricarbonyl	Strem
Tetramethylammonium iodide	Aldrich
Tetraethylammonium iodide	Aldrich
Tetrapropylammonium iodide	Aldrich
Tetrabutylammonium iodide	Aldrich
Triethylaluminum	Texas Alkyls

2. GC Chemicals	Source	Grade
Hexadecane	Aldrich	99%
Tetradecane	Aldrich	99%
Octadecane	Aldrich	97%
Eicosane	Aldrich	99%
n-Hexane	BDH	Reagent
n-Docosane	Aldrich	99%
Dodecane	Aldrich	99%
Octane	Aldrich	Gold Label
Decane	Aldrich	Gold Label
Dichloromethane	Terochem	Reagent
Carbon Disulphide	BDH	Green Label
Pentane	MCB	Spectroquality

APPENDIX D

LIST OF INSTRUMENTATION USED

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- Perkin-Elmer Infra-red Spectrophotometer 283
- Varian Model 3700 Gas Chromatograph with HP 3390A Integrator
- Varian Model 2440 Gas Chromatograph with modified injection port to allow on-column injection with HP 3390A Integrator
- Varian 5000 Liquid Chromatograph with UV and RI detectors
- Perkin-Elmer R32 NMR Spectrometer - 90 MHz
- Perkin-Elmer R12B NMR Spectrometer - 60 MHz
- Brüker WM250 NMR Spectrometer - 250 MHz
- Hitachi Perkin-Elmer 115 Molecular Weight Apparatus
- National Appliance Co. Model 5831 Vacuum Oven
- Finnigan 3300Gas Chromatograph/Mass Spectrometer with PDP 11/23 based data system